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FHWA/IN/JHRP-96/4
Final Report

ENVIRONMENTAL BIOASSAY EVALUATION OF FOUNDRY WASTE RESIDUALS

K. Chad Chastain
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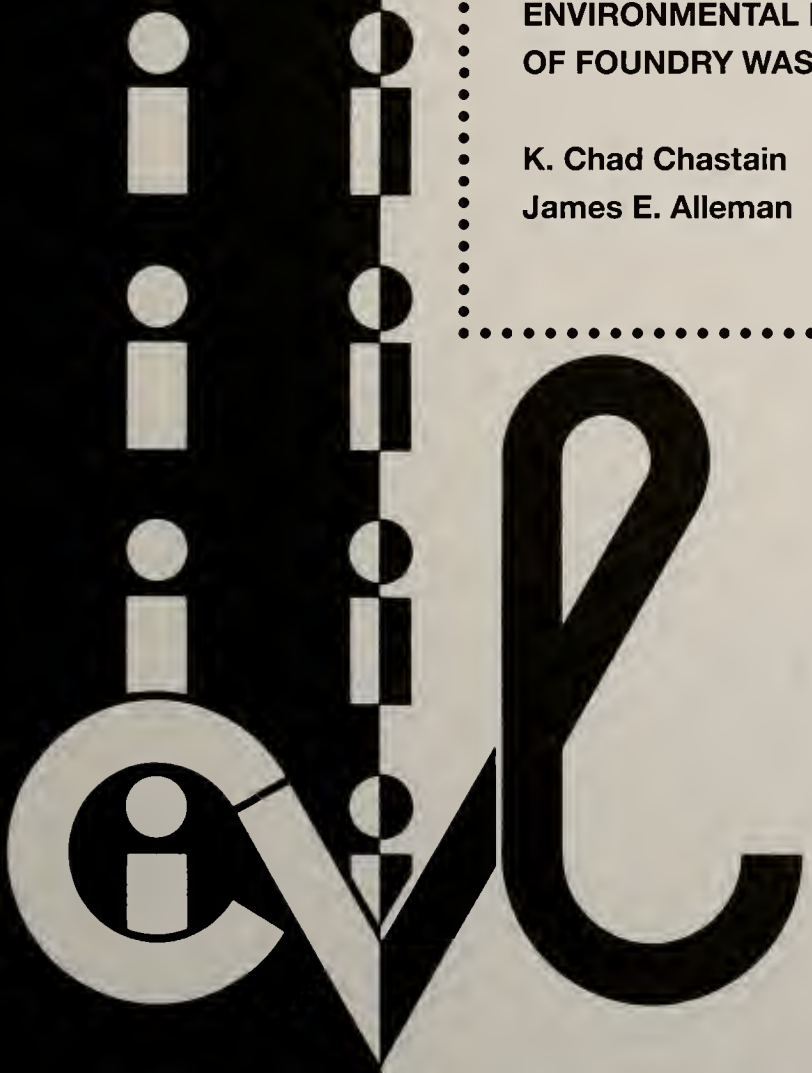

PURDUE UNIVERSITY

FINAL REPORT

ENVIRONMENTAL BIOASSAY EVALUATION of FOUNDRY WASTE RESIDUALS

FHWA/IN/JHRP-96/4

by

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16. Abstract

Although the constructive reuse of foundry residuals represents a decidedly beneficial goal with distinct economic and environmental benefits, potential end-users are nonetheless reluctant to use these residuals, given an inherent concern about potential unforeseen environmental liabilities. Results of foundry residual leachate characterization to date strongly suggest that many ferrous foundries are discarding sands whose quality is fully amenable to their future use with embankment construction and related high-volume highway development activities.

In order to provide additional assurance as to the environmental impact of foundry residual reuse, the Microtox™ bioassay has been used to quantify the response of living organisms (e.g., the microorganism, *Vibrio fischeri*) to ferrous foundry residual leachates. This response has been compared with the response of the organisms to 'virgin' sands used in the foundry industry and as construction materials.

Leachates from the majority of the ferrous foundries tested caused less inhibition of light production by the Microtox™ bacteria than did virgin sands. Taken literally, it appears that these sands are truly, "cleaner than dirt." Furthermore, for these sands, no real differences were seen between system sands and fresh or aged waste sands. In a limited number of instances, however, there were clear and consistent indications that the tested waste foundry sands had released a contaminating toxin or toxins into the leachate waters, thereby resulting in a quantifiable depression in observed microbial activity.

This innovative bioassay test appears to offer an efficient and expedient approach to 'fingerprinting' foundry locations for which constructive waste sand reuse could subsequently be pursued without undue concern about negative environmental impacts. Additionally, there appears to be a correlation between casting process (e.g., core binders, casting size, casting temperature) and bacterial impact, such that foundries could potentially utilize bioassay response data in focusing pollution prevention efforts.

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IMPLEMENTATION REPORT

This research focused on the application of microbiological assays to foundry sand residuals, with the objective of utilizing these residuals as raw construction materials for Indiana Department of Transportation (INDOT) highway development projects. In the course of this study, a commercially available bacterial bioassay (Microtox™) was demonstrated to be capable of identifying sands which can be recommended for beneficial reuse in these INDOT projects, and was used to thoroughly characterize one specific foundry's wastes. The following suggestions are, therefore, being provided as a means of implementing and extending this research effort.

- **Field-scale Foundry Sand Embankment Demonstration Project**

A field-scale demonstration project which constructively employs foundry residuals represents a logical opportunity with which this material qualification protocol (i.e., based on Microtox™ bioassay characterization) could be further evaluated. Indeed, the Indiana Department of Transportation has recently started one such highway embankment project near Butler, Indiana (S.R. 206) which used approximately 50,000 cubic yards of waste foundry sand provided and trucked on a *gratis* basis by a regional foundry. In parallel with this latter project, INDOT has sponsored a complementary research project which includes both environmental and geotechnical pre-construction testing and site characterization, testing of materials and site monitoring during the period of construction, and post-construction monitoring. Two adjacent embankment sections were installed at this site, one built with foundry sand and the other using virgin sands, such that any leachates generated by the foundry wastes can be compared to leachate released from the nearby 'control' section which contains virgin sand.

- **Field-scale Foundry Sand Flowable Fill Demonstration Project**

Field demonstration projects using foundry wastes for controlled low-strength material ('CLSM,' or flowable fill) aggregate are also recommended, particularly based on the INDOT-funded research effort completed by Bhat and Lovell (1996). Such projects could be relatively easily monitored, and the option of using waste foundry sand in flowable fill may be especially attractive to foundries which do not produce the large quantities of waste foundry sand required for highway projects.

- **Continued Laboratory Experimentation**

Concurrent with these field study areas, additional laboratory research should follow three directions. First, application of additional bioassay protocol(s) to foundry residuals would complement and validate the use of the Microtox™ bioassay for these wastes (NOTE: this effort is being launched as part of the experimental project for S.R. 206, as was discussed above). Second, further investigation of residuals from additional foundries would allow the creation of specifications which INDOT can use to routinely accept or reject specific sources or stockpiles of waste foundry sands based on bioassay test results. Third, additional study of the mechanisms of microbial inhibition caused by some foundry sand leachates would provide INDOT with the ability to rapidly make preliminary estimates of foundry waste quality based on foundry processes, without the need for extensive testing. This information could also assist foundries to monitor and/or adjust their own processes such that beneficial reuse of foundry residuals can be made more universally possible.

CHAPTER 1

INTRODUCTION

Beneficial reuse of ferrous foundry sands for highway construction activities represents an extremely attractive goal for a wide variety of technical, environmental, and economic reasons. Indeed, the following listing covers a diverse group of apparent benefits which might be realized with this sort of mutually beneficial reuse strategy:

- **First**, ferrous foundry sands have already been extensively tested in regard to their geotechnical properties, such that their engineering suitability for highway embankment, and other high-volume applications has largely been validated,
- **Second,** the environmental testing currently required with this material has, to date, also been quite positive with respect to its chemical-specific leachate behavior,
- **Third,** 'constructive' applications could yield significant savings in landfill space due to the sheer magnitude of these wastes,
- **Fourth,** the low-cost (and perhaps even *gratis*) availability of these sands should also provide significant cost savings for end-users as compared to procuring locally available (natural) sand materials, and
- **Fifth,** the contributing ferrous foundries should realize a sizable cost savings as compared to their current expenditures for sand disposal at local landfills.

In addition, we must acknowledge the undeniable fact that operational and historical precedents also exist in which 'reuse' has long been a key issue for foundry operations and their waste sands. Setting aside the fact that the feedstock metals brought into these plants are themselves largely waste materials (i.e., engine blocks, used rail lines, etc.), internal recycle of core and molding sands is an important aspect of any plant's overall survival in an extremely competitive business. Fresh raw sand is typically brought into these plants on a daily basis as makeup for spent residuals, but these sands will almost certainly pass through many cycles of internal reuse before finally being discarded. At the same time, constructively-minded disposal strategies for these waste sands were a commonplace occurrence since the early part of the century. In fact, many of our nation's foundry towns could justifiably claim that their foundations were supported by these very wastes.

However, in spite of these apparent benefits and historical precedents, current and future end users will frankly have to address the legal reality of environmental liabilities which any waste materials

might impose. Indeed, state-level Department of Transportation officials contacted within the Midwest (i.e., including Wisconsin, Ohio, Iowa, Illinois, and Indiana) commonly characterize the issue of liability as a significant, if not dominant, hurdle which has yet to be resolved in the particular case of foundry sand reuse. This specter of being connected (legally and financially) to the title of, 'potentially responsible party,' is understandably worrisome.

This circumstance admittedly reflects a conservative mindset tinged with the legal uncertainties inherent to material transfers of this sort. While these sands may truly be "*cleaner than dirt*," as typically claimed by foundry representatives, potential end users are nonetheless compelled to develop their own '*reasonable engineering certainty*' regarding long-term acceptability.

This high-volume 'waste' consequently has an inherent appeal as a potential candidate for 'constructive reuse applications.' However, even though the available data suggest that these wastes are suitably safe, there is an implicit concern about hidden risks not covered by the criteria currently used to calibrate and classify environmental quality.

As a result, a considerable amount of environmental testing has been conducted on these spent foundry residuals in order to characterize their expected levels of contaminant release. In particular, a large number of tests have been published covering metal leachate levels under both acidic and neutral pH conditions. These leachate results have generally been quite favorable, at least with gray and ductile iron foundry sands, with the observed levels of contamination for all of the significant heavy metal criteria being less (and commonly far lower) than the established 'hazardous' levels.

At the same time, a number of additional tests have been reported in the literature for a complementary range of additional inorganic and organic parameters, including such species as cyanide, fluoride, sulfate, sulfide, and a wide range of organics (e.g., phenols, naphthalene, etc.). Here again, the reported results suggest that many of these sands are acceptably 'clean' in terms of producing leachates with low contaminant levels.

The fact remains, though, that the informative value of these leachate evaluations is tempered by a concern that relatively few parameters are actually being measured. Indeed, the listing of regulated criteria applied to industrial residuals is barely more than a few dozen parameters in length, beyond which certainly lies a vast range of unregulated chemicals for which concerns about environmental contamination might be similarly justified. The range of these tests, though, has frankly been constrained for a variety of reasons. Unquestionably, the costs associated with environmental compliance represent an important limiting factor. However, the underlying issue is moreso a reflection of our present inability to defensibly define tolerable levels of risk for all chemical species, let alone mixtures thereof.

Given the current mood about incurring unforeseen liabilities with waste materials, a strong argument can then be made that further steps must be taken in order to more accurately verify the environmental suitability of these residuals. In particular, the use of bioassay tests as a surrogate indication of potentially harmful environmental impacts looks attractive.

Limited testing of this sort has been conducted with a group of foundry sands at Penn State University (Westervelt, 1988; Regan and Contos, 1991) using both bacterial (i.e., Microtox™) and invertebrate (i.e., *Daphnia*) bioassay methods. Admittedly, the results of these latter analyses were somewhat confusing. There was some indication that inhibitory impacts were being measured during their limited testing program, but these authors were frankly not sure whether the problem was due to true toxins or interfering, yet truly non-toxic, sensitivities inherent to their testing methods (e.g., caused by zinc, etc.). Whatever the case, their efforts did set a precedent for the overall concept of using bioassay strategies to qualitatively evaluate spent foundry sands.

Further evaluation of ferrous foundry residuals using analogous bioassay methods consequently represents an extremely beneficial research topic. Even if large-scale chemical-specific testing of these complex wastes had not been cost-prohibitive, these individual tests would provide no information about potential complications caused by problematic synergisms. Whole sample bioassay testing, though, would provide an all-encompassing characterization of this material's potential to impose a negative impact on environmental quality, thereby generating a far more useful assessment of the waste's fundamental suitability for reuse.

Pursuant to these concerns, therefore, the Indiana Department of Transportation has pro-actively supported a series of recent research projects through Purdue University designed not only to address geotechnical performance issues but also environmental impacts. Extending beyond chemical-specific leachate testing such as the TCLP test, therefore, our Purdue research group subsequently developed a completely new, state-of-the-art foundry sand leachate generation and testing protocol which provides a biological assessment (i.e., 'Microtox™ bioassay') of foundry wastes in terms of their environmental character.

This relatively simple and inexpensive test was correspondingly designed to evaluate each waste sand in comparison to the bioassay response (Microtox™) to virgin materials. The leachate solutions used to conduct these tests were obtained by contacting individual sands with a saline solution (at a respective volumetric ratio of 1:4) for 18 hours.

As documented within this report, the *'cleanliness'* of the sands obtained from many foundries was readily evident when their results were compared to virgin, natural materials. However, in a limited number of instances, there were clear and consistent indications that certain tested waste foundry sands had released an undesired chemical substance(s) into the leachate waters which resulted in a

quantifiable depression in the observed Microtox™ activity. Although this innovative bioassay analysis will not identify either the composition or concentration of these contaminants, the test will serve as an extremely useful calibration tool with which we can extend our level of knowledge beyond the currently regulated criteria. Indeed, this procedure will provide a biological characterization which will complement the chemical-specific testing (i.e., and already mandated), effectively fingerprinting foundry locations suitable for constructive waste sand reuse.

CHAPTER 2

OBJECTIVES

2.1 OVERVIEW

This project was developed to evaluate the use of bacterial bioassay techniques for characterizing waste ferrous foundry sands as a complementary means of qualifying environmental behavior. Microtox™ testing was used for the majority of these bioassay analyses. In addition, a completely new '*Nitrotox*' bioassay test (which uses commonplace, nitrifying soil bacteria) developed at Purdue University was also used on a limited basis to develop a secondary perspective on the bioassay status for these waste sands. These tests were then collectively applied to a range of foundry waste residuals taken from existing operations within the State of Indiana. These foundries and their tested sands were intended to reflect the typical nature of materials produced within this industry.

Representative sand samples were voluntarily contributed by nearly a dozen Indiana foundries, including not only iron foundries but also one aluminum and one steel foundry. For most of these locations, several samples were obtained over an extended period of time in order to calibrate the extent of chronological variation in their bioassay behavior. These tests also covered a variety of foundry sand forms, including system, fresh, and aged waste sands, as well as virgin (i.e., natural) sands.

Overall, this effort was intended to evaluate and demonstrate the utility of bioassay testing as a potential analytical resource for routine material evaluation. In the particular case of foundry sand residuals, this study attempted to fingerprint 'questionable' sands whose repetitive behavior would recommend against, or preclude, their involvement with waste reuse activities.

2.2 SPECIFIC RESEARCH OBJECTIVES

- To adapt an existing, commercial bioassay technique (i.e., Microtox™ technique) to the specific evaluation of waste foundry sands.
- To experimentally develop a routine protocol with which the Microtox™ bioassay could be used for testing waste foundry sand leachates.
- To evaluate the Microtox™ bioassay behavior of waste sands produced at regional ferrous foundry operations.
- To complete these latter Microtox™ bioassays over an extended chronological period, thereby characterizing the inherent level of variation for these tests.

- To develop a similar Microtox™ bioassay evaluation of natural sands against which the waste sands could be qualified.
- To develop and apply a second, parallel bioassay procedure (i.e., the so-called '*Nitrotox*' test) for characterizing these waste sands.
- To conduct a preliminary evaluation of the organic contaminants which might be associated with waste foundry sands.
- To collectively evaluate these tested waste sands in terms of their apparent bioassay performance as compared against the virgin sands.

CHAPTER 3

TECHNICAL BACKGROUND

3.1 PERMANENT PATTERN/EXPENDABLE MOLD CASTING OVERVIEW

Foundry sand is utilized in permanent pattern/expendable mold casting processes. In these processes, molten metal is poured into a mold made of sand which has been shaped and hardened to withstand the pressure and heat derived from the heated metal. After the metal has cooled, the sand is separated from the casting and recycled. Although foundries go to great lengths to recycle as much sand as possible, some foundry sand must be wasted each cycle due to the physical and chemical breakdown of the sand and from the necessity of using virgin sand for some parts of the mold.

3.2 PERMANENT PATTERN/EXPENDABLE MOLD CASTING PROCEDURES

When casting metal in this manner, the first pieces created are the patterns. These pieces are fashioned in the shape of the desired casting, and can be made from wood, plastic, or metal. The pattern is usually made in two parts, corresponding to the top and bottom parts of the mold. If one were to imagine casting a sphere of metal, the two pattern pieces would look like hemispheres sitting on flat plates.

The next step is the fabrication of the two parts of the mold. Box shaped containers are filled with sand, the pattern pieces are placed against the sand surface, and the sand is compacted by impact, squeezing, vibration, air flow, or vacuum (Clegg, 1991). The pattern is then removed, and the two parts of the mold can be fastened together to create the cavity into which the metal is poured.

Many castings require additional sand pieces called cores. These pieces are added inside the mold cavity to produce the inner shape of the casting. After the metal has been poured and has cooled, the mold containers are opened, the core and mold sand breaks apart and is removed from inside and around the casting, and the metal piece can be further processed. Figure 1 on the following page provides a schematic display of the general procedures involved with preparing a permanent pattern, expandable casting mold.

3.3 PERMANENT PATTERN/EXPENDABLE MOLD CASTING MATERIALS

Most permanent pattern/expendable mold systems use "green sand" processes--not meaning that the sand is green, but that water has been added to the sand, which is used while still damp (Foundry Management & Technology (FM&T), 1993). Clays are also added to the sand; when the clays, which are hydrous alumino-silicates such as illites, kaolinites, and montmorillonites, are hydrated, surface interactions between the sand and clay particles produce the bonding forces. Other additives, such

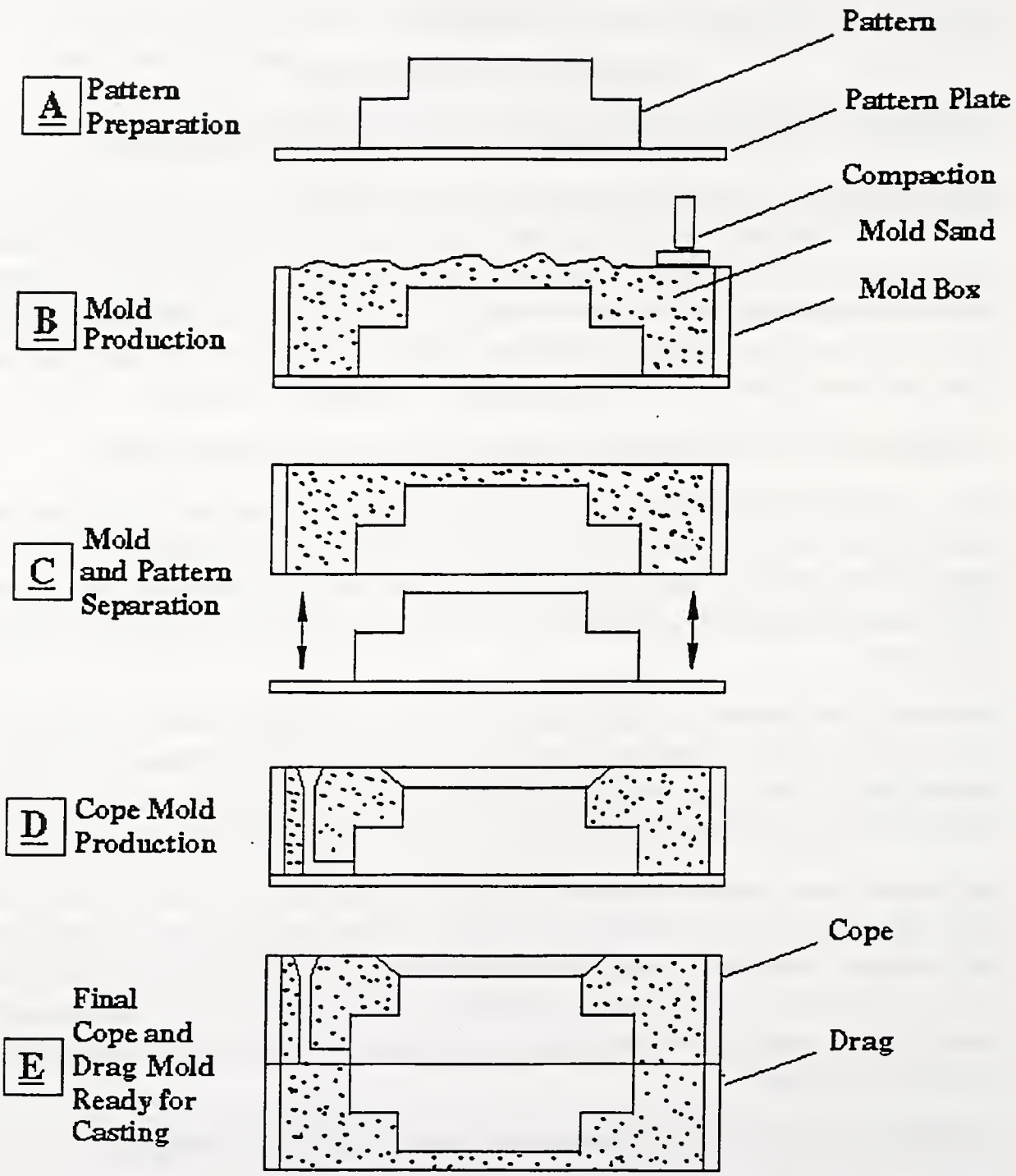


FIGURE 1: Schematic of Permanent Pattern Mold Preparation

(Redrawn from Clegg, 1991)

as sea coal, starch, pitch, asphalt, and petroleum distillates may be used to control strength, deformation characteristics, surface finish, and defects (Clegg, 1991).

When the metal is poured and the sand reaches temperatures above 100 °C (212 °F), free moisture is driven off. Many organics, such as those found in sea coal, are then volatilized. Above approximately 1,100 °F (600 °C), the combined water which forms the sand-clay and clay-clay bonds begins to be driven off; all water is gone at temperatures above 1470 °F (800 °C) (FM&T, 1993). After the casting has cooled, the sand can be separated (usually by shaking/vibratory mechanisms), and recycled: fine particles are removed, lumps of sand are broken up, any remaining metal is removed, and the sand returned to the stockpile of system sand (FM&T, 1993). As much as 90 to 95 percent of the sand is recycled after each casting.

Core pieces, on the other hand, are made exclusively from virgin sand. This is necessary because the chemicals used as binders for the cores are not effective with clay-coated sand. Although there are many varieties of chemical binder systems, the majority of binders used in Indiana ferrous foundries are mixtures of organic chemicals. Organic binders can be grouped into three categories: cold set (also called no-bake), cold box, and hot box. Most of these binders utilize one or more binder chemicals and a catalyst or hardener which, when added, promotes the binding reaction(s). Cold set binder systems utilize liquid catalysts, and reactions occur at room temperature. Cold box binder systems utilize gaseous catalysts, again at room temperature. Hot box binder reactions take place at high temperatures (150 to 300 °C; 300 to 570 °F) (Clegg, 1991).

A short summary of the different binder types is given below, in Table I. For more detailed information, see the Appendix. Silicate-CO_2 binders, alumina phosphate binders, and furan/furfuryl alcohol based binders, in particular, have been promoted as being environmentally friendly due to the lack of toxic volatiles created by core making and casting processes (Bambauer, 1993; FM&T, 1993).

Table I. Summary of Selected Permanent Pattern/Expandable Mold Casting Processes

Type	Name	Binders and Additives
Inorganic Option	Greensand	Clays, water, starch, and sea coal
	Alumina phosphate	Aluminum phosphate resin, and metal oxide hardeners
Cold Set/No-Bake Options	Furan	Furfuryl alcohol resins, urea, phenol, and aryl sulfonic acids
	Phenolic urethane	Phenol formaldehyde resin, isocyanates, and liquid amines
	Sodium silicate	Liquid sodium silicate and liquid organic ester
Cold Box Options	Phenolic urethane	Phenol formaldehyde resin, polymeric isocyanate, and gaseous amine
	Silicate-CO_2	Liquid sodium silicate, coal dust, clays, and CO_2 gas
Heat Activated Options	Hot box	Furfuryl alcohol or phenolic resin, urea, formaldehyde, and acid catalyst
	Shell molding	Phenol formaldehyde resins, calcium stearate, Vinsol, iron oxide, and hexamethylene tetra-amine
	Air set	Various oil resins
	Core oil	Unsaturated oil resins, oxygen sources, and solvents

3.4 FOUNDRY WASTE MATERIALS

Foundry solid wastes can include refractories, system sand, core sand, annealing and cleaning room wastes, slag, coke ash, scrubber discharge, baghouse dust, and floor sweepings (Boyle and Ham, 1979). By volume, the majority of foundry wastes are comprised of waste foundry sands (WFS). Since this project's focus is WFS reuse, the environmental characteristics of WFS will be considered in detail.

3.5 APPLICABLE SOLID WASTE REGULATIONS

Although foundry sands are recycled to as great an extent as possible within a foundry, sand is still wasted at a rate on the order of ½ ton sand per ton of metal cast (Filip, 1993). In Indiana, waste

foundry sands are regulated under Section 329 of the Indiana Administrative Code (IAC), Article 2, entitled "Solid Waste Management." Part 3 of Rule 9 within this code (i.e., 329 IAC 2-9-3) specifies criteria used to characterize non-hazardous industrial solid wastes, also termed restricted wastes. In this characterization, the concentrations of several chemicals are measured in leachate produced from the sands. Standard methods to produce leachate from solid wastes were first developed in an attempt to simulate the environment in a municipal landfill; wastes are designated hazardous if they leach concentrations of listed chemicals greater than levels set by regulators. This idea was extended to restricted wastes: a first group of chemicals, which are metals, must be measured in leachate generated with the Extraction Procedure Toxicity (EP Tox) test (329 IAC 3-6-6) or the Toxicity Characteristic Leaching Procedure (see Code of Federal Regulations – 40 CFR 261-Appendix II; 7/1/92 edition), and a second group of chemicals, which includes additional metals, inorganics, and organics, must be measured in leachate generated with the leaching method test. This latter procedure (i.e., the 'Indiana Leaching Method' test) is the same as the EP Tox test, except that no acetic acid is added to the leaching solution. The characterization criteria are respectively listed in Tables II and III.

Table II: Restricted Waste Criteria for Parameters Using Leachate Generated with the EP Tox Test or TCLP

Contaminant Parameter	Concentration (milligrams per liter)			
	Type IV	Type III	Type II	Type I
Arsenic	≤0.05	≤0.5	≤1.25	<5.0
Barium	≤1	≤10	≤25	<100
Cadmium	≤0.01	≤0.1	≤0.25	<1.0
Chromium	≤0.05	≤0.5	≤1.25	<5.0
Lead	≤0.05	≤0.5	≤1.25	<5.0
Mercury	≤0.002	≤0.02	≤0.05	<0.2
Selenium	≤0.01	≤0.1	≤0.25	<1.0
Silver	≤0.05	≤0.5	≤1.25	<5.0

In general, restricted wastes must be disposed of in what are termed "Restricted Waste Sites." These sites must conform to specifications which are more stringent than those met by sanitary landfills but are not as difficult to achieve as those for hazardous waste landfills (329 IAC 2-10-4). Certain exceptions apply, however. Waste foundry sands meeting Type IV standards are excluded from regulation under 329 IAC 2 (329 IAC 2-3-3). In addition, WFS meeting Type III standards are excluded from regulation under 329 IAC 2 when legitimately used, including as a base for road building (329 IAC 2-3-1 (14)). The vast majority of ferrous WFS meet Type III or IV criteria, and are thus acceptable for use as road base construction materials according to Indiana regulations.

Table III: Restricted Waste Criteria for Parameters Using Leachate Generated with the 'Indiana Leaching Method' Test

Contaminant Parameter	Concentration (milligrams per liter) Type IV	Type III	Type II	Type I
Barium	≤1	≤10	≤25	*
Boron	≤2	≤20	≤50	*
Chlorides	≤250	≤2,500	≤6,250	*
Copper	≤0.25	≤2.5	≤6.25	*
Cyanide, total	≤0.2	≤2	≤5	*
Fluoride	≤1.4	≤14	≤35	*
Iron	≤1.5	≤15	*	*
Manganese	≤0.05	≤0.5	*	*
Nickel	≤0.2	≤2	≤5	*
Phenols	≤0.3	≤3	≤7.5	*
Sodium	≤250	≤2,500	≤6,250	*
Sulfate	≤250	≤2,500	≤6,250	*
Sulfide, total	≤1	≤5	≤12.5	*
Total dissolved solids	≤500	≤5,000	≤12,500	*
Zinc	≤2.5	≤25	≤62.5	*

*: Testing not required

3.6 RELATED REGIONAL STATE REUSE ACTIVITY

3.6.1 General

Stepping back in time several decades, if not centuries, sand recycling has long been a key factor for successful foundry operations, both within plant operations and with waste emissions. For any given plant, mold and core sands have been routinely recycled until their particle size or properties were no longer conducive to their desired performance. At that point, system sands would be mixed with fresh make-up to replace a wasted fraction of spent material which might then be constructively used for local fill in borrow pits and other marginal land areas.

Well into the 1970's, waste foundry sands were widely viewed as a reusable resource, particularly given the absence of contemporary (and inherently stringent) regulatory requirements. With a veritable mountain of this waste being discarded each month around the country, one could well have expected to quickly hear about its environmental impact had it carried even the slightest hint of either an acute or chronic negative quality. However, community complaints about these waste sands in the past, at least for the gray and ductile iron business, were nominal in volume, almost to the point of being nil. In all fairness to these wastes, therefore, we should acknowledge the fact that their retrospective behavior has given us little cause for concern about their future impact. And yet, faced with the unknown specter of potential liability, potential users must still proceed with considerable care in selecting and qualifying these wastes for reuse applications. The status of WFS reuse differs

from state to state, depending on regulators as well as potential users. Accordingly, a state-by-state 'roadmap' of WFS regulations and reuse status across the United States is provided in the following sections.

3.6.2 Pennsylvania

Contact-1: *Dr. Ray Regan, Penn State University, Dept. Civil Engrg.: 814-863-0601*

Contact-2: *Dan Oman, RMT Inc.: 610-834-0490*

Pennsylvania is perhaps closer than any state to allowing general use of WFS. Among others, Dr. Ray Regan of Penn State University has been working since the mid-1980's to facilitate WFS use in highway and other projects. To this end, two foundry-owned companies have sited and opened disposal facilities for the purpose of monofilling foundry wastes. Tipping fees charged at these landfills are $14/ton, significantly less than the local municipal landfill rate of $25/ton. These two companies are the Process Recovery Corporation (PRC), in eastern Pennsylvania, and the Allegheny Recovery Corporation (ARC), in western Pennsylvania. The first such company (PRC), with its 33 participating foundries, has even secured a permit for the specific use of waste sand as fine aggregate in road construction. In a recent application approximately 25 tons were utilized for road construction by the Pennsylvania Department of Transportation (PenDOT).

Although the ARC, which has 25 member foundries, is not at present allowed similar WFS reuse, a group of 37 foundries has applied to the Pennsylvania Department of Environmental Protection (DEP) for a general WFS reuse permit. This group includes foundries associated with PRC, ARC, and others. The DEP permit, when granted, will allow much more broad use of WFS, even including use in plant nurseries.

The requirements stipulated by the permit include measurement of 22 metals and 4 organics in WFS leachates. In the past, Pennsylvania foundries have found it difficult to pass leachate concentration limits for iron and manganese. Now, however, the DEP has allowed the leachate to be generated by a procedure called the Synthetic Precipitation Test rather than the TCLP; this is expected to result in lower leachate iron and manganese levels. Organics to be measured include naphthalene, benzene, toluene, and xylene, depending on the binder chemicals used. Most laboratories will test for all four, as it would be difficult to specify the exact binders used for each sample.

The DEP is reportedly ready to sign the permit application, and PenDOT is "*raring to go*" with a 2000-ton demonstration project (Regan, 1996). Once the permit is granted, the foundries will then be faced with the logistical challenges of obtaining sufficient sand for the project and economically transporting it to the project site. Nevertheless, the granting of the general use permit is seen as a major step toward common use of WFS by all foundries in Pennsylvania.

3.6.3 Michigan

Contact: *Larry Heinig (Michigan DOT: 517-322-5657)*

Placement of waste foundry sand was reported to be an accepted practice in Michigan, particularly around the Saginaw area which has a considerable volume of these spent sands. However, this proactive stance shifted dramatically following a singular instance in which these waste sands were found to have released a phenolic leachate contaminant into adjacent waters. This discovery actually developed as a secondary observation to a far larger, unrelated post-construction problem, but the end result was that Michigan's DOT decided to specifically preclude any future use of these sands with an appropriately written exclusive specification.

Within the past few years, however, Michigan's foundries have decided to follow the precedent set in Pennsylvania (see prior section's discussion). Fifteen foundries in the western part of the state banded together to form the Resource Recovery Corporation of West Michigan (Contact: David Walborn, 616-737-0102) on a 3-acre site (possibly increasing to 6 acres). This recycling facility, under construction as of January 1996, is intended to facilitate the collection, classification, reclamation, processing, storage, and distribution of spent foundry residuals. When operational (spring or summer of 1996), it will be able to provide an outlet for foundry wastes to be used in asphalt manufacture and landfill daily cover requirements. Additionally, this effort represents a positive effort by the cooperating foundries to opportunistically position themselves for waste reuse opportunities as they develop in the future.

In spite of these efforts, though, the current Michigan DOT perspective on reusing these sands still remains negative due to expressed fears about liability complications, largely stemming from fears about unidentified contaminants. The foundries themselves also recognize and bear these same fears, to the point where their recovery operation intends to have each contributing foundry categorize and separate their wastes, such that this segregation can be maintained throughout the entire materials handling and storage process. Although this would in fact protect each foundry from some potential liability, the effort necessary to maintain barriers between each waste (akin to a hazardous waste landfill situation) will bring additional costs.

3.6.4 Wisconsin

Contact: *Bruce Fister (Wisconsin DOT: 608-246-7945)*

As will be described in Chapter 4, researchers at the University of Wisconsin at Madison have been investigating the environmental quality of foundry sands since the mid-1970's, soon after the United States' initial efforts at solid waste regulation. Professors Robert Ham and William Boyle have enthusiastically sought out opportunities to demonstrate the environmental viability of using foundry

wastes for construction projects, and one such experimental demonstration was implemented by Wisconsin's Department of Transportation using ~10,000 cubic yards of sand for a highway bridge project. An extensive monitoring program was developed for this site, with lysimeters being installed to procure '*in-situ*' leachates for subsequent testing, and the corresponding results proved to be extremely positive.

In spite of this compelling precedent, however, Wisconsin's DOT is currently in a 'holding pattern' due to concerns regarding liability. They previously applied for a liability waiver from the Wisconsin Department of Natural Resources (DNR), but the request was disallowed. Wisconsin's DOT has consequently considered pursuing an alternative course of action, whereby they (i.e., DOT) would establish so-called 'partnering agreements' with the involved foundries through which these parties would assume joint liability. At this point, therefore, it does not appear that Wisconsin's DOT has any use immediate plans for using foundry wastes.

3.6.5 Illinois

Contact: *Tom Shootsbach (Illinois DOT: 217-782-7213)*

The present mood about reuse of waste foundry sand by the Illinois Department of Transportation could best be described as 'vague' and 'unresolved.' As with their neighboring states, this organization also carries distinct concerns about liability problems which might arise in the future.

One unique step taken by this State was the stipulation that recyclers must furnish 'Material Safety Data Sheets' (MSDS) for each group of materials which they handle. However, in the particular case of foundry operations and residuals, it does not appear that these sorts of MSDS sheets have ever been considered, let alone prepared, for waste foundry sands. In turn, the prospects for recycling this industry's wastes are rather moot.

3.6.6 Ohio

Contact: *Bill Edwards (Ohio DOT: 614-752-5272)*

Although the State of Ohio's Department of Transportation has indicated that they are "*not that excited*" about the current prospects for reusing waste foundry sand, their State recently (November 7, 1994) passed legislation to facilitate the beneficial use of non-toxic bottom ash, fly ash, and spent foundry sand (Ohio EPA Policy 0400.007: "*Beneficial Use of Non-Toxic Bottom Ash, Fly Ash, and Spent Foundry Sand and Other Exempt Wastes*"). According to this new policy, non-toxic materials within each of these three categories are exempt from regulation as hazardous or residual solid waste if they pass certain criteria. The policy specifically states that beneficial reuse of these materials shall not require a permit by the Ohio Environmental Protection Agency.

Several beneficial reuse applications were cited within this new policy (e.g., flowable fill, anti-skid materials, etc.), and it also appears that foundry sands are being added as a raw substrate within cement kilns. In the case of flowable fill, though, the DOT does not yet have any relevant specifications. They are reportedly trying to produce usable versions at the present time. Furthermore, these waste foundry sands do not meet the Ohio DOT's present specifications as either a soil or granular material, and concerns were expressed about its content of silty fine material and related behavior problems.

Ohio's new policy qualifies permissible reuse applications according to leachate quality, taking into consideration not only TCLP results but also the release of chlorides, phenol, cyanide, pH, fluoride, sulfates, total dissolved solids (TDS), and specific conductance. (**NOTE**: these latter additions to the TCLP group are essentially the same as associated with Indiana's Leaching Method parameters; however, the Indiana criteria also includes yet another group of chemical parameters, including: barium, boron, copper, iron, manganese, nickel, sodium, sulfide, and zinc).

3.6.7 Iowa

Contact: *Jim Rost (Iowa DOT: 515-239-1798)*

In May, 1994, Iowa's Environmental Protection Commission passed an amendment to their administrative code for "*Reuse of Solid Waste*" (see Iowa Administrative Bulletin (IAB) 4/13/94, pg. 2078-2780), which establishes their State's seemingly progressive criteria for reuse of waste foundry sand. In short, this ruling (Amended Rule 567-108) allowed several different beneficial reuse activities without any permit whatsoever (daily landfill cover, road construction, etc.) for those wastes whose TCLP values were less than or equal to 90% of the Federal RCRA leachate classification limits (see CFR 261.24).

The proposed beneficial uses for which no permit was required included: daily cover at a landfill, road ballast, construction or architectural fill, dike or levee construction, fill base for roads, road shoulders, parking lots, or other similar uses, and any other beneficial use upon written notification by a foundry person. Setting aside this legislative circumstance, though, Iowa's DOT has expressed concerns about assuming unknown liabilities with these sorts of materials. Iowa's DOT specifications apparently do have an option for a contractor to come back with a proposal to use foundry sands. However, Iowa DOT was reportedly hesitant to use these materials due to their concerns about contaminants, including metals, especially for those applications in close proximity to groundwaters. Their primary interest at this time, therefore, was in using waste foundry sand with flowable fills.

CHAPTER 4

PRIOR CHEMICAL CHARACTERIZATION OF FOUNDRY WASTES

In the late 1970's, prior to the development of the EP Tox and TCLP tests, researchers W.C. Boyle and R.K. Ham of the University of Wisconsin at Madison developed a shake flask procedure for leaching spent foundry sands and subsequently measured organic carbon, chemical oxygen demand (COD), phenol, cyanide, fluoride, sulfates, and pH in leachates from wastes from several ferrous foundries (Boyle and Ham, 1979; Ham *et al.*, 1981). For some of these tests, the component parts (e.g., system sand, core butts, core room sweepings, slag, dust collector discharge, scrubber discharge, refractories, and cleaning room waste) of these wastes were tested as well as the composite waste stream. It was seen that COD measurements in the separate constituents provided an reasonable estimate of COD concentrations in the mixed wastes; phenol levels, however, were often much higher in the composited wastes than was predicted by phenol release by the individual constituents. Lysimeter studies based on actual rainfall amounts yielded maximum concentrations of 14-120 mg/L organic carbon, 75-290 mg/L COD, 25-400 µg/L phenol, 80 µg/L cyanide, 3-120 mg/L fluoride, 30-1,220 mg/L sulfates, and pH ranges of 7.2 to 10.0 in leachates from the three ferrous sands studied. Phenol and COD levels were lower than those observed in the shake flask tests. In shake flask and lysimeter testing, metal concentrations were seen to be very low.

During the mid-1980's, this same research group conducted an evaluation of the potential for leaching of organics from WFS (Ham *et al.*, 1993**a**). Nine binder and core making processes, representing the major procedures used in the casting industry, were chosen, including: phenol formaldehyde, phenolic urethane, furan hot box, furan no-bake, phenolic ester, core oil, phenolic isocyanate, alkyd isocyanate, and furan warm box. Those foundry wastes which would likely contain organics, including excess system sand, core butts, and core room sweepings, were tested. The TCLP leaching procedure was used as it is the standard EPA method for toxicity characterization. Most of the organics identified by gas chromatography/mass spectroscopy (GC/MS) analysis were quantified using gas chromatography with a flame ionization detector (GC/FID).

Organic chemicals which were detected were deemed worthy of comment if they were included on one of four regulatory lists promulgated by EPA. These were (1) the priority pollutant list, which identifies chemicals which are environmental hazards and are found in water (88 compounds, excluding pesticides and PCBs); (2) the TCLP chemical list (38 compounds, excluding pesticides); (3) drinking water standards; and (4) a list included with the proposed solid waste disposal facility criteria under Subtitle D of the Resource Conservation and Recovery Act (RCRA), intended to apply

to the release of hazardous constituents from nonhazardous waste disposal facilities. The chemicals which were detected in leachates from any of the nine foundry waste types and were included on any of these lists are included in Table IV.

As shown by these data, no organic chemical was found at a concentration of above 1 ppm, nor were any of the chemicals found at high enough concentrations to be considered hazardous. The only chemicals exceeding the standards set in any of the above lists were benzene, which was

found at concentrations higher than the DWS maximum contaminant level (MCL) in leachates from three sands, and tetrachloroethene, which was found at a concentration equaling a "trigger level" calculated to be used where DWS have not been established. Each of these standards, however, was designed to be applied to groundwater or drinking water rather than applied directly to leachate; it would be unlikely that concentrations of these compounds in groundwater would ever reach the abovementioned standard levels. Core oil and phenolic urethane binder systems leached the greatest number of organic chemicals.

Table IV: Organic Chemicals Measured in Waste Foundry Sands

Chemical Compound	Quantitation Limit Limit (ppb)	Maximum Concentration (ppb)
Acetone	100	200
Benzene	2	11
Benzoic Acid	N.D.	400
2,4-Dimethylphenol	20	120
Ethylbenzene	0.4	24
1,1,1-Trichloroethane	2	49
Naphthalene	1	480
2-Methylnaphthalene	1	320
Phenol	30	540
Dimethylphthalate	40	61
Phenanthrene	30	38
Tetrachloroethene	2	7
Toluene	0.5	61
Cresols	30	150
Xylenes	0.4	140

Organics were also measured in groundwater collected at four Wisconsin landfills containing only foundry wastes. No organic species was observed to have a concentration above the quantitation limit; several compounds at trace levels were tentatively identified. These included tetrachloroethene, naphthalene, chloroform, 1,1,1-trichloroethane, 1,2-dichloroethane, and di- and trichloroethene. It was suggested that some of these findings may have been due to laboratory error. As in previous work (Blaha *et al.*, 1985), concentrations of groundwater contaminants did not correlate well with leachate test concentrations.

The variability of WFS leachate characteristics has also been studied (Krueger *et al.*, 1989). Three types of foundry wastes were investigated: system sands, because they comprise the greatest amount of foundry waste; core butts, because it was considered to be the most heterogeneous, and baghouse dust, because is was considered to contain the highest metal concentrations while remaining relatively heterogeneous. The leaching tests used were the EP Toxicity and a deionized water leaching test which followed EP Toxicity test procedures except that no attempts were made to control the solution pH. The parameters analyzed were cadmium, chromium, copper, iron, lead, manganese, zinc, cyanide, phenol, and fluoride.

Variability due to three sources was examined. These were (1) sample collection and preparation (leaching), (2) laboratory analytical procedures, and (3) variations in waste quality over time. While the analytical procedures made only a small contribution to data variability (the average coefficient of variation was only 6.4%), the procedures used to riffle, split, and leach the sands contributed a potentially large source of error (the average coefficient of variation was 45%). It was statistically uncertain whether the EP leaching contributed more or less variability than the deionized water leaching. Among five constituents which were measured over a two month period (copper, iron, zinc, cyanide, and fluoride), significant temporal variation was also observed: coefficients of variation averaged 42% for the baghouse dust, 57% for the core butts, and 47% for the system sand.

A landmark, three-year study on contamination stemming from WFS use was performed on Wisconsin sands and soils by the Wisconsin-Madison research group in the early 1990's (Ham *et al.*, 1993**b**). Sands from three foundries were used to generate leachate according to TCLP and American Foundrymen's Society (AFS) Laboratory Leach Test protocols. Characterization of these leachates included testing for twelve metals, eight other inorganic chemical groups, and bulk parameters including alkalinity, conductance, hardness, pH, total dissolved solids (TDS), and total organic carbon (TOC).

The results from the sands were compared with soils considered typical of agricultural or construction soils. None of the sand or soil samples were found to be hazardous according to RCRA. Causes of potential adverse impacts were classified into two groups: top priority parameters, which had average values significantly greater in WFS leachates than in virgin soils and at least one sample which exceeded drinking water standards (DWS); and second priority parameters, which met one but not both of the above conditions. The top priority parameter of greatest concern was iron, which was found at concentrations higher than the DWS in TCLP leachates from all three foundries and in AFS test leachate from one of the foundries. Additional top priority parameters included fluoride, for which the secondary DWS were exceeded; pH; and TDS. Second priority parameters included arsenic, chromium, copper, fluorides, iron, manganese, pH, TDS, zinc, phenolics, and sulfates.

A field study was then designed and implemented, in which groundwater and leachate were collected from test piles throughout a one and one-half year period. The amount of leachate generated was small due to the low permeabilities of the WFS piles. Arsenic was found at concentrations above the DWS level in leachate from WFS and natural soil piles. Manganese and TDS exceeded the DWS at times in leachate from WFS and natural soil piles. Chloride and pH exceeded DWS in WFS leachate on one date each; chromium, cadmium, and lead exceeded the DWS in leachates from natural soil piles only. Iron exceeded the DWS in only one WFS leachate. Based on these data, the researchers concluded that the WFS used in this study performed comparably to natural soils.

CHAPTER 5

BIOASSAY CHARACTERIZATION of WASTE FOUNDRY SANDS

5.1 TECHNICAL OVERVIEW AND BACKGROUND

Chemical-specific leachate testing, as has been covered in the previous sections, has several advantages, including the ability to measure very low levels of contaminants; the opportunity to utilize well-understood and accepted protocols; acceptable comparisons with standards, other wastes, and even unrelated risk factors; and potentially low cost. It is particularly applicable to industrial wastes whose constituents are known and which vary little over time. When measuring the toxicity of samples which are not well characterized, however, another method is sometimes used: the bioassay. Simply put, a bioassay is a test which directly measures the effect of a particular environment on a living organism. Ideally, the effects on the organisms can be correlated with risks to humans or other environmentally sensitive species more effectively than can simple concentrations of contaminants.

This is partly due to the fact that in contaminated environments, more than one chemical compound or species is often present. The effects of the combined toxicants on living organisms are not necessarily simply additive. Toxicity can be antagonistic, or less than the sum of the individual toxic effects; additive; synergistic, or greater than the sum of the individual toxicities; or neutral, in which the effect of one or more species is masked or negated by the presence of other compounds (Dutka and Kwan, 1982). Interaction between contaminants or other environmental variables cannot generally be predicted *a priori.* Thus, an advantage of a bioassay is that this interaction can be detected.

Bioassays can be separated into acute tests and chronic tests. An acute test measures the response of the organism over a short period of time--usually a few minutes to a few hours. The response measured is usually death or inactivation of the organism. Chronic tests, on the other hand, measure the effects of an organism's environment over a period comparable to its lifetime. Detection of cancers, mutations, or changes in the organism's reproductive abilities can be used as endpoints for chronic toxicity tests. Chronic tests are generally more sensitive to environmental pollutants, but are much more costly, time-consuming, and labor-intensive.

5.2 GENERAL HISTORICAL PRECEDENTS FOR BIOASSAY EVALUATIONS

The concept of using bioassays measurements to qualify the presence of potentially harmful contaminants is not a modern development. In fact, these sorts of tests have been in use for many centuries, if not millennia. For example, during ancient times, servants were asked to 'sample' food items prepared for royalty, assumedly hoping to negate any risk of poisoning either by intent or accident. Following a similar line of reasoning, the Romans were known to evaluate the health of

populations living adjacent to the reservoirs which supplied their aqueducts, and in those instances where outbreaks of sickness were observed they would temporarily discontinue drawing these waters.

Somewhat more recently, another bioassay test was routinely conducted with miners working deep underground during the latter century. These miners were understandably concerned about the quality of the air supply, but lacked adequate analytical equipment with which they could actually monitor a parameter like oxygen content. However, in lieu of measuring the air and its related chemistry, they would carry bird cages with them on their way to work. Parakeets placed in these cages would then serve as acute indicators for the quality of their air supply.

In modern times, bioassays have been used for many different applications. For example, a wide variety of products manufactured for human use and consumption (e.g., cosmetics, pharmaceuticals, etc.) are routinely pre-tested and certified to obviate any harmful impact on humans, in terms allergenic response, dermatitis, etc. Bioassay testing has also become a commonplace requirement for qualifying the acceptability of wastewater effluents based on a so-called 'whole effluent toxicity' analysis (i.e., 'WET'; see related discussion in the following section).

5.3 REGULATORY STATUS FOR ENVIRONMENTAL BIOASSAY EVALUATIONS

At present, bioassay testing is standard requirement for most wastewater treatment operations, wherein these effluents must be proven to be suitably non-toxic for their permitted discharge. These bioassay requirements, as are included within a facility's National Pollutant Discharge Elimination System (NPDES) permit, reflect a major shift in federal regulatory policy over the past quarter century. Prior to the 1970's, effluent testing was essentially limited to 'chemical-specific' analyses, covering a limited group of inorganic and organic parameters. While these regulated criteria are still written into each permit, the U.S. EPA recognized a need to restrict and control the discharge of toxins as a whole...and that effluent limitations on specific compounds would not necessarily provide an adequate measure of protection. Their implicit concern was that the chemical-specific requirements would not provide such safeguards against unregulated toxins or for those compounds whose impacts are additive, synergistic, or antagonistic. Several different types of bioassays have subsequently been developed, with acute and chronic fish and invertebrate options most commonly being stipulated. The resultant expectation is that the permitted effluent should not exhibit a toxic response during its bioassay evaluation at levels of dilution commensurate with local conditions under worst-case conditions (i.e., with a permissible dilution level of one-quarter the receiving water body's 10-year low flow value). In the event that a toxic condition is consequently identified, these facilities are then tasked with the responsibility to perform 'toxicity reduction evaluations' (TRE's) in order to identify the culprit compounds. The responsible chemical(s) can then assumedly be traced back to the originating source and subsequently eliminated by appropriate enforcement action.

Extending beyond these wastewater operations, environmental bioassay testing has recently assumed a considerable measure of interest...although its actual regulatory application has not yet become commonplace. Bioassay measurements of sediment toxicity likely represents the closest analogy to the sort of residuals testing (as opposed to waters) (i.e., foundry sands) being addressed within this project. Indeed, the recent literature on toxicity testing includes considerable evidence of sediment bioassay analyses using not only the Microtox™ procedure but also a related proprietary option called Mutatox™, which intends to identify the presence or absence of potential contaminant mutagens as opposed to chemical toxins. Many of these latter investigations appear to have similar goals, whereby semi-solid materials such as dredged residuals are being evaluated with regard to prospective disposal options and their prospective impacts. While bioassay testing is solely mandated for wastewater effluent compliance, therefore, similarly motivated measurements are being developed and applied for a range of environmental samples.

5.4 NON-BACTERIAL BIOASSAY OVERVIEW

Over the past several decades, a rather diverse range of bioassay options have been developed for determining the presence of toxins. While higher life forms, including mammals such as rats, mice, etc., may commonly be used in conjunction with food and drug testing, fish are typically the most advanced organisms used with environmental tests. However, given the cost and complexity of using fish (e.g., fathead minnows, rainbow trout, etc.), the practice of bioassay testing has recently shifted towards less complex and less costly organisms, including invertebrates, algae, fungi, and bacteria. A specific set of two of these latter protocols has been emphasized with this project, which in both cases were intended to provide a relatively fast assessment of a given waste foundry sand's apparent environmental quality. The following section provides further details regarding the available options and benefits for these 'bacterial' procedures.

5.5 BACTERIAL BIOASSAY OVERVIEW

Microbial bioassays have some decided advantages over animal and plant testing (Blaise, 1991). Microorganisms are relatively easy to culture, and testing is generally less labor-intensive than when higher life forms are used. Due to their quick growth rate and small size, a statistically significant number of microorganisms can be economically used, negating the effects of individual variation. Microbial bioassays can be conducted rapidly, requiring a few minutes to a few hours as opposed to days, weeks, or even months. Relatively small sample volumes are necessary. Finally, using microorganisms avoids the delicate and emotional issue of bioassay testing procedures which might be linked to animal abuse concerns. The difficulty arises when one attempts to correlate the effects of environmental variables on such organisms with the possible effects on humans or other target species or environments. This is not a problem limited to microorganisms the validity of risk

assessment based on plant and animal data is an issue which will probably be debated for decades, if not centuries. Perhaps, however, the difficulty of relating human risk to effects on the microbial level is exacerbated by the fact that microorganisms and humans are so far apart on the scale of complexity and intelligence. One way to get around this obstacle is to make conservative estimates of risk. To do this, microbial bioassays must be designed to be more sensitive to the particular environmental variable(s) than are humans or other target species.

Efforts to discover the optimal bioassay microorganism or protocol has lead to the development of many different bioassay tests. The majority of microbial bioassays are acute tests utilizing bacteria. Such assays can be grouped into two categories: bacterial assays, in which some measurement of activity based on whole-cell processes is made, and biochemical or enzymatic assays, which measure the activity of one or more specific bacterial enzymes. Bacterial assays include those based on bacterial survival and growth (Dutka & Kwan, 1982; Trevors, 1986), motility (Dutka & Kwan, 1982; Sanchez *et al.*, 1988), respiration (King and Dutka, 1982; Elnabarawy, 1988; Alleman, 1986; Kong, 1993; Sun, 1994), nitrification or nitrogen cycling (Williamson and Johnson, 1976, 1981; Alleman, 1986; Mathes & Schulz-Berendt, 1988; Arvin *et al.*, 1994), the production of minute quantities of heat (Jolicoeur and Beaubien, 1986), bacterial membrane integrity (Bitton *et al.*, 1988; Fort *et al.*, 1994) and gas production by anaerobic organisms (Owen, 1979). The most well-known bacterial bioassays are the Ames test, which measures the mutagenicity (not toxicity) of a sample (Ames *et al.*, 1975; Ames, 1979; April, 1990), and the bioluminescence test Microtox™, about which more will be said later. Biochemical assays have measured the effects on enzymes including dehydrogenases (Catallo, 1990; Bitton, *et al.*,1986; Trevors, 1984; Bitton and Koopman, 1986; and Bitton and Koopman, 1992), adenosine triphosphatases (ATPases) (Xu, 1987), esterases and phosphatases (Bitton and Koopman, 1992), urease (Jung, 1994), and the biosynthesis of galactosidase, glucosidase, and tryptophanase (Logue, 1989; Bitton and Koopman, 1992; Reinhartz, 1987; Dutton *et al.*, 1990 **a** & **b**).

5.6 REVIEW OF SELECTED BACTERIAL BIOASSAYS

5.6.1 Bioluminescence Bioassays

5.6.1.1 General Analytical Concept

The Microtox™ bioassay was the first commercial acute bacterial bioassay, and is today the *de facto* standard with which other microbial bioassays are compared. It was first introduced in 1979 by Beckman Instruments (Bulich, 1979); at present, it is sold by Microbics Corporation, Carlsbad, California. Since its introduction, Microtox™ protocols have been developed for samples of widely varying toxicity, ranging from contaminated soils to drinking water. (see Figure 2).

OTPIONAL MICROTOX™ TESTING PROTOCOLS

High _____ Sample Toxicity Level _____ Low

Solid-Phase Test
(Microtox Acute Test)
- Soil
- Sediment

Basic Test
(Microtox Acute Test)
- Pure Compounds
- Septage
- WWTP Influent

90% Basic Test
(Microtox Acute Test)
- Process Wastestreams
- IPP Discharges
- Toxicity Baseline Studies

Inhibition Test
(Microtox Acute Test)
- TRE Testing
- Storm Water Runoff
- WWTP Effluent Screening
- Toxicity Source Testing

Comparison Test
(Microtox Acute Test)
- Final WWTP Effluent
- Final TRE Testing
- Final Storm Water Runoff
- Drinking Water

Chronic Test
(Microtox Chronic Test)
- WWTP Effluent
- Fate and Effect Studies
- Compliance Assurance
- Drinking Water

FIGURE 2. Overview of Microtox™ Testing Protocols

The Microtox™ system utilizes the luminescent marine bacteria *Vibrio fischeri.* The enzymatic systems present in these organisms produce light when the appropriate environmental conditions are present (Nealson and Hastings, 1979; Ribo and Rogers, 1988). When the bacteria are negatively impacted, as by a toxin, the light they produce decreases. This decrease can be accurately measured, providing a quantitative determination of toxicity. Researchers have explored the biological effects of pollutants on this bacteria's ability to produce light for at least three decades (Serat, 1965).

5.6.1.2 Bioluminescent Bioassay Performance Overview

As the *Vibrio fischeri* organisms originated in a marine environment, the Microtox™ system was first applied to aqueous samples. To date, Microtox™ aqueous toxicity data has been gathered for over 1600 individual compounds (Kaiser and Palabrica, 1991). In addition, aqueous organic chemicals, municipal wastes, complex industrial wastes, and leachates from hazardous wastes have all been analyzed with Microtox™ tests (Munkittrick *et al.*, 1991). More recently, contaminated sediments have been studied, both by measuring the toxicity of sediment extracts and by using a solid-phase test in which the organisms come into contact with the sediment directly.

Advantages of the Microtox™ test, including low cost, low time requirements, simplicity, and reproducibility. Potential weaknesses include a lack of sensitivity to certain compounds such as ammonia and cyanide, the necessary addition of 2% salt solution, pH constraints, and potential problems with samples that are colored or have significant turbidity, suspended solids, or hardness (Qureshi *et al.*, 1982; Qureshi *et al.*, 1984).

5.6.1.3 Bioluminescent Bioassay Performance with Known Chemical Mixtures

Dutka and Kwan (1982) assayed three organic chemicals, five metals, and mixtures thereof with the Microtox™ system. It was observed that total toxicity could not be easily characterized as additive, neutral, synergistic, or antagonistic but depended on the contaminants used and even on the concentrations of the chemicals. Qureshi *et al.* (1984), measuring the response to binary combinations of six metals, obtained similar results, possibly attributed to changes in metal speciation due to oxidation or reduction of the metals. A mathematical model was proposed by Ribo and Rogers (1990) to predict the toxicity of chemical mixtures based on the toxicities of the individual constituents. Assumptions upon which the model was based included (1) that the toxicants would have similar mechanisms of actions and (2) that the toxicity was additive. A good correlation was observed between model predictions and experimental results for mixtures of chlorinated phenols. Additional studies utilizing mixtures of dissimilar chemicals are needed to further validate the model.

5.6.1.4 Correlations between Microtox™ and Other Bioassays

The Microtox™ test has been compared with many other bioassay protocols, including those using

bacterial, invertebrates, fish, amphibian, mammal, and plant species (Kaiser and Palabrica, 1991). Walker (1988) compared the relative sensitivity of 234 tests, using over 149 species, to phenol. It was seen that the Microtox™ assay was among the more sensitive species to the acute effects of phenol.

Microtox™ data were exhaustively reviewed by Munkittrick *et al.* (1991), who found that for pure organics and complex effluents, the Microtox™ assay was generally at least as sensitive as rainbow trout, *Daphnia*, species, and fathead minnows. Compounds which were exceptions to this trend included cyanide, chloroform, and phenol. For inorganics and organics including insecticides and herbicides, pharmaceutical wastes, and lipophilic contaminants, Microtox™ was generally less sensitive than the other species. Ammonia was singled out as having little effect on the Microtox™ organisms relative to the other species. It was noted that one study separated municipal wastes into soluble and insoluble constituents; Microtox™ was much more sensitive to the soluble constituents (Slattery, 1988).

Using toxicity data for 200 individual chemicals, a high collinearity has been demonstrated between Microtox™ toxicity and fathead minnow 96-hour lethality. Such relationships have also been demonstrated with Goldorfe fish and zebrafish, both of which have been used as standard test species in Europe. The least collinearity with Microtox™ toxicity has been seen with results with rat bioassays; this is not surprising, as rat bioassays have not been shown to correlate well with any other biological endpoint (Kaiser and Palabrica, 1991).

In attempts to understand more fundamentally, or at least to predict, such interspecies similarities and differences, relationships between toxicity and chemical parameters (e.g., Quantitative Structure-Activity Relationships, or QSARs) have been examined (Ribo and Kaiser, 1983; Blum and Speece, 1991; Blum and Speece, 1992). These parameters include molecular connectivity, molar volume, polarity/polarizability, hydrogen bond characteristics, and octanol/water partitioning tendencies. Due to the complexity of these living systems, however, QSARs are much more valid when comparing toxicities of groups of similar chemicals than when comparing toxicities of chemicals which have significantly different molecular structures.

5.6.1.5 Bioluminescent Bioassay Performance with Complex Mixtures and Effluents

Samples of complex mixtures, including surface waters, municipal wastewaters, and industrial wastewaters and effluents have been tested with the Microtox™ assay (Bulich, 1984; Qureshi *et al.*, 1984; Sanchez *et al.*, 1988; Logue *et al.*, 1989, and Levi *et al.*, 1989). In general, the Microtox™ bioassay has a sensitivity level on the same order as other common bioassays. In one study, for example, eighty-two Brazilian industrial effluents were analyzed using Microtox™, *Spirillum volutans*, *Daphnia similis*, and several other bioassays (Sanchez *et al.*, 1988). Microtox™, *Spirillum*

volutans, and *Daphnia similis* results agreed well and allowed the researchers to rapidly screen for toxic discharges. Levi *et al.* constructed an on-line Microtox™ bioassay which provided the ability to monitor the toxicity of river water influent to a drinking water supply intake.

In short, the sensitivity of the Microtox™ bioassay is comparable to that of most other commonly used species, and is great enough to be of value in most toxicity testing scenarios. The optimal strategy, however, is the use of more than one bioassay species, even including species of widely differing biological complexity, in a "battery of tests" approach (Dutka and Kwan, 1988). In this way, the different tests can be used in a complementary fashion.

5.6.1.6 Bioluminescent Bioassay Performance with Solids and Hazardous Wastes

The toxicity of hazardous wastes and solids, including soils and sediments, presents a challenge beyond that of aqueous wastes: sample generation. Leachate testing is one available option. Calleja *et al* (1986), for example, investigated the toxicity of leachates from pesticide and electroplating sludge wastes to Microtox™ and *Daphnia magna.* Although the authors reported that "*good agreement in toxicity assessment*" was obtained, the *Daphnia* species were more sensitive to pesticide leachates, and were more uniformly sensitive over time to leachates from electroplating sludge wastes.

Testing of contaminated sediments has often involved analysis of pore water as well as extractions from dewatered sediment samples. A sediment study by Dutka *et al.* (1988), for example, performed ten biochemical and bacterial tests, including Microtox™, on samples of water and samples of sediment extracted with high-purity water. It was determined that no single test was effective at predicting toxicity. In a related study, Dutka and Kwan (1988) sediments extracted with water displayed no toxicity to Microtox™, bacterial ATP-based tests, and a bacterial motility test, but did result in positive toxicity to *Daphnia magna.* When the sediments were extracted with the organic solvent dimethyl sulfoxide (DMSO), however, toxicity was observed in the bacterial tests. A sediment bioassay (Schiewe *et al.*, 1985) investigated methanol, acetone, DMSO, dichloromethane and ethanol for use in extracting pollutants from the sediments. It was determined that ethanol extraction was effective and less toxic than the other solvents. Highly significant correlations were made between Microtox™ toxicity and the sum of concentrations of aromatic hydrocarbons and between Microtox™ toxicity and the sum of concentrations of naphthalenes. A significant correlation was made between Microtox™ toxicity and the sum of the concentrations of chlorinated hydrocarbons. A Detroit River sediment study compared the toxicity of sediment pore water using Microtox™ and *Daphnia magna* 48-hour lethality tests (Geisy *et al.*, 1988); in this case, the Microtox™ assay generally proved more sensitive, although the researchers recommended using a battery of tests rather than using Microtox™ alone. Pastorok and Becker (1990) reached similar

conclusions when comparing organically-extracted sediments from Superfund sites in Puget Sound using Microtox™ and six other sediment toxicity bioassays.

Leachate toxicity testing has also been utilized to monitor detoxification of treated wastes and sites. Aprill *et al.* (1990) applied Microtox™ testing to evaluate the effectiveness of an *in situ* bioremediation process used to clean up a site contaminated with wood preserving and petroleum wastes. It was seen that, although chemical analyses demonstrated decreasing levels of contaminants, pore water and soil extract toxicity did not decrease after one year of treatment. The toxicity was attributed to toxic metabolites produced by the bioremediation processes. These byproducts would not necessarily have been detected by leachate chemical analyses; toxicity testing was recommended as a method for assessing detoxification efficacy. Microtox™ testing was used in a related manner by Casarini *et al.* (1991). In this study, the amount of hazardous wastes which could be treated through land application was estimated as that which did not cause detectable soil water toxicity.

The alternative to leachate or extract toxicity testing is the analysis of the solid itself. A recently developed Microtox™ assay (Tung *et al.*, 1990; Bulich *et al.*, 1992) provides this opportunity. Initially, the solid or sediment is combined with the bacterial suspension for a period of time. The suspension is then filtered, separating the solid from the bacteria; the light output can be measured as with the aqueous phase test. In spite of potential sources of error such as loss of bacteria or introduction of solids during the filtration step, this new protocol is seen as an important new tool in the microbiological testing of solids and sediments. Efforts to calibrate this new test using synthetic soils, as well as real soil and sediment samples, are being undertaken at this time.

5.6.1.7 Bioluminescent Bioassay Summary

The Microtox™ assay, based on the bioluminescence of the bacteria *Vibrio fischeri*, has been extensively tested with organic and inorganic chemicals, complex wastes and effluents, sediments, soils, and hazardous wastes. It has been used for toxicity screening of drinking waters and contaminated sites, process monitoring, and for determination of environmental discharge permit compliance. No one bioassay, or even one type of bioassay, will fit all needs, but of the multitude of bioassays available, The Microtox™ is one of the most rapid, most well understood, least expensive, and least labor-intensive.

5.6.2 Dehydrogenase Bioassays

5.6.2.1 General

Dehydrogenase assays focus on one small group of enzymes that are part of the electron transport system (ETS), the biochemical pathway which allows cells to use oxygen to produce energy. In the late 19th century, it was discovered that a group of chemicals known as tetrazolium salts had

reduction potentials similar to substances being reduced through normal ETS activity. When cells are actively respiring, tetrazolium salts present can be simultaneously reduced, forming compounds called formazans. Fortuitously, the formazan compounds have noticeably different colors and solubilities than their oxidized counterparts. This change provides a simple method for detection of respiration by active cells.

There are two types of tetrazolium compounds, 1-H-tetrazolium salts and 2-H-tetrazolium salts. Only 2-H-tetrazolium salts are used in biological systems (Seidler, 1991). These can be subdivided by the number of tetrazolium groups in the compound; mono- and ditetrazolium salts have been utilized in toxicity testing. These include TTC (2,3,5-triphenyl-2*H*-tetrazolium chloride), INT (2-(*p*-iodophenyl)-3-(*p*-nitrophenyl)-5-phenyl-2*H*-tetrazolium chloride), NBT (nitroblue tetrazolium; 3,3'-(3,3'-dimethoxy-4,4'-biphenylylene)-bis-(2-*p*-nitrophenyl -5-phenyl- 2*H*-tetrazolium chloride), and MTT (3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2*H*-tetrazolium bromide) (Bitton and Koopman, 1986). Although TTC has been used to measure dehydrogenase activity in bacterial cultures, soils, sediments, and sludges, its reduction is inhibited or prevented by the presence of oxygen (Bitton and Koopman, 1986; Seidler, 1991). ETS activity has been measured with NBT reduction, but no toxicity tests *per se* have been developed (Bitton and Koopman, 1986).

5.6.2.2 INT-based assays

INT is colorless and soluble; INT-formazan (INTF), the reduced form of INT, is deposited as insoluble red crystals inside actively respiring cells. Several reports of INT-based toxicity testing, most by researchers at the University of Florida, have been made. As early as 1984, Koopman et al. reported on the assessment of toxic inhibition of filamentous bacteria in activated sludge by way of INT reduction. One can determine gross biological activity by lysing (breaking apart) the cells, extracting the INTF crystals with a solvent, and measuring the absorbence of the resulting solution spectrophotometrically (termed DHA_e, or dehydrogenase assay--extraction). Alternatively, one can distinguish between active and inactive cells by looking at individual cells with a microscope; those containing red INTF crystals are active, while inactive cells contain no crystals (termed DHA_e, or dehydrogenase assay--counting). In the Koopman *et al.* study, DHA_e data correlated well with DHA_e results in the filamentous bacteria studied (*Sphaerotilus natans*), as well as with oxygen uptake rate (OUR), a conventional method of determining bacterial activity. A later study (Kim *et al.*, 1994) also correlated DHA_e data with oxygen uptake and ATP activity, finding the INT-based assay to be as sensitive as OUR and more sensitive than ATP measurements.

Trevors (1984) used INT to directly measure ETS activity in soils and sediments. An aqueous solution of INT was added to soil and sediment samples; subsamples were removed periodically and the INTF was extracted with methanol. The effects of pentachlorophenol (PCP) and mercury (Hg)

were observed and relationships between toxicity and temperature, oxygen status, and substrate addition were noted.

The University of Florida group developed a direct INT hydrogenase assay (DIDHA) (Bitton *et al.*, 1986) which avoided extraction requirements. A double-beam spectrophotometer was used to determine ETS activity in cellular suspensions based on intercellular INTF. Response of *Pseudomonas alcaligenes* to copper, zinc, cadmium, phenol, *alpha*-naphthol, and five herbicides using the DIDHA assay was similar to results from an INT extraction-based assay. It was seen that clay and humic acid particles had the effect of reducing pesticide toxicity, probably due to adsorption of the organic pesticides onto the particles.

Heavy metal toxicity to activated sludge was the focus of a study by Anderson *et al.* (1988). Tetrachloroethylene and acetone to were used to extract INTF and results were compared with OUR data. The INT assay appeared to be slightly more sensitive to copper and zinc, have similar sensitivity to cadmium and lead, and be slightly less sensitive to mercury and nickel than OUR measurements. It is noted that tetrazolium-based bioassays might be more sensitive to metals than OUR-based assays, but substantially less sensitive to certain classes of toxicants, especially those which uncouple electron transport from oxidative phosphorylation. Examples of such uncoupling include cyanide and phenolics.

5.6.2.3 MTT-based assays

While INT is clear, MTT has an obvious yellow color. MTT-formazan is insoluble and has deep blue/purple color. Ryssov-Nielsen (1975) used MTT to analyze the inhibition of activated sludge by zinc, mercury, potassium cyanide, 2,4-dichlorophenol, and 2,4-dichlorophenoxyacetic acid (2,4-D). Although metal- and 2,4-dichlorophenol-amended cultures followed a typical pattern of inhibition, the cultures to which potassium cyanide was added appeared to be stimulated by low levels of MTT. The author attributed the cyanide-related stimulation to "artificial MTT respiration" utilizing MTT as an electron acceptor (e.g., taking the place of oxygen) for the cytochrome oxidase enzyme.

Another series of MTT assays was initiated by Mossman (1983) with mammalian cells (i.e., mouse lymphoma and T cells). A 96-well spectrophotometric plate reader was used to analyze up to 96 samples at a time, facilitating rapid testing using small sample volumes. Several researchers studying mammalian cells have since modified Mossman's test, using hamster lung fibroblasts and human cells such as lymphocytes, lung cancer cells, and skin keratinocytes.

Incubation time with the MTT has varied between 2 and 24 hours, and incubation time with the solvent has ranged from 1 minute to approximately 16 hours. The choice of chemicals used to dissolve the MTT-formazan has included acid isopropanol, ethanol, sodium dodecyl sulfate, mineral

oil, and dimethyl sulfoxide (Tada *et al.*, 1986; Denizot and Lang, 1986; Carmichael *et al.*, 1987; Chapdelaine, 1989; Hansen *et al.*, 1989; Ciapetti *et al.*, 1993).

5.6.2.4 Summary

Dehydrogenase assays are not as well-known or as fully developed as is the Microtox™ assay. They do, however, present several potential advantages over other tests. First, as dehydrogenase assays employ relatively common and inexpensive analytical instruments (e.g., spectrophotometers and/or microscopes), little or no initial expenditures are necessary for their use. Second, one could utilize a vast array of bacteria; the nitrifying bacteria used in this study are simply and inexpensively grown. Third, with a tool such as a 96-well plate reader, many samples can be performed at one time. The effectiveness of the tests would depend on the sensitivity of the particular bacteria chosen and on the specific protocol developed, but, in general, dehydrogenase assays show great promise in the search for rapid, inexpensive, sensitive risk assessment techniques.

5.7 DOCUMENTED BIOASSAY EVALUATIONS OF WASTE FOUNDRY SANDS

The only report of waste foundry sand toxicity testing is detailed in a thesis by W.W. Westervelt, a graduate student of Professor Raymond Regan's at The Pennsylvania State University (Westervelt, 1988). Samples from 33 Pennsylvania foundries were collected and composited into four categories: sand wastes from all of the foundries, sand wastes from only non-ferrous foundries, baghouse dust from all foundries, and sludge from all foundries. These composite samples were mixed in quantities proportional to the output of the several foundries; the composite sand, for example, consisted of 95% ferrous foundry waste and 5% non-ferrous foundry waste. Unfortunately, wastes from ferrous foundries were not isolated for testing; nor was it noted that only greensand process wastes were used. Each of the four sample types were tested for bulk and leachate chemical concentrations and for leachate toxicity. Four different leachate types were used: saturated paste leachates, 5:1 and 20:1 water:solid ratio leachates, and TCLP leachates. Organisms used for determination of leachate toxicity were the Microtox™ *Vibrio fischeri* and *Daphnia magna.* Bulk analysis revealed that silica comprised over 95% of the sand wastes and approximately 75% of baghouse dust and sludge wastes. Additional major cations included aluminum, calcium, iron, potassium, magnesium, sodium, and zinc. Lead was also found at a concentration of approximately 3.5% in the sludge samples. Other than lead in the sludge samples, only trace levels of the metals included in primary drinking water standards (arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver) were detected. Sludge samples leached the greatest amount of aluminum, cadmium, nickel, lead, sulfate, and chloride. Baghouse dust leached the greatest amount of iron. Manganese and zinc were highest in non-ferrous foundry sand leachate. The composite sands leached the fewest metals.

Daphnia magna acute toxicity was generally limited to the non-ferrous sand samples. 5-minute

Microtox™ toxicity results are listed in Table V on the following page. The unit used is toxic units (TU), defined as the reciprocal of the dilution that causes 50% inactivation of the test population. It was seen that after 5 minutes, the composite sand samples exhibited the greatest Microtox™ toxicity for each leachate. That toxicity level remained relatively constant over the 30-minute time period, indicating that the source of toxicity was probably organic, as the organisms tend to display effects produced by organic compounds within five minutes. After 15 and 30 minutes, the greatest Microtox™ toxicity by far was displayed by the non-ferrous sands. An increase in toxicity after five minutes suggests metal contamination, as metal-related inhibition often takes longer than 5 minutes to develop.

Literature toxicity data for *Daphnia* species and Microtox™ organisms were compared with leachate metal concentrations. Zinc and, to a lesser extent, cadmium and copper were identified as potential toxins to *Daphnia* and Microtox™ in non-ferrous sand leachate samples. No other leachate samples contained metals at levels which suggested significant metal toxicity.

Table V: Microtox™ toxicity of foundry wastes *(after Westervelt, 1988)*

	5-minute results (TU)		
Leachate Source	Saturated Paste	5:1 water:solid	20:1 water:solid
Composite sand	12.5	7.4	2.7
Non-ferrous sand	8.3	2.9	1.6
Baghouse dust	2.1	0.7	0.4
Sludge	1.7	0.6	0.4
	15-minute results (TU)		
Leachate Source	Saturated Paste	5:1 water:solid	20:1 water:solid
Composite sand	11.7	6.9	2.1
Non-ferrous sand	53.3	7.7	3.9
Baghouse dust	2.5	0.8	0.4
Sludge	1.5	1	0.6
	30-minute results (TU)		
Leachate Source	Saturated Paste	5:1 water:solid	20:1 water:solid
Composite sand	12.6	7.6	2.1
Non-ferrous sand	263.7	18.3	--
Baghouse dust	3.4	1	--
Sludge	1.6	2	0.7

These hypotheses were tested by adding EDTA, a compound which chelates (captures) metals and prevents them from causing toxicity, to foundry waste samples. As shown by the Microtox™ data in Table VI, composite sandtoxicity increased slightly upon addition of EDTA, while non-ferrous sands to which EDTA had been added were less toxic than the unaltered sands after five minutes and remained at that low level throughout the 30 minute test.

These findings confirmed the indications of toxicity source: organics in the composite sand samples and metals in the non-ferrous sand samples.

Table VI: Microtox™ toxicity of foundry wastes upon addition of EDTA *(after Westervelt, 1988)*

Leachate Source	Microtox™ EC_{50} (TU)		
	5-minute	15-minute	30-minute
Composite sand	12.8	11.5	11.9
Composite sand with EDTA	17.2	14.3	14.7
Non-ferrous sand	3.2	8.1	17.9
Non-ferrous sand with EDTA	0.89	1.0	1.1

The organics utilized in casting systems are associated with greensand binder additives (sea coal, starch, pitch, asphalt, and petroleum distillates) and with core binders (see Appendix I). These would be found in ferrous and non-ferrous systems; the amount of organics remaining on the sand would depend on melting temperature, binder type, casting size and shape, and a multitude of other site-specific variables. Toxic metals would probably only be found in appreciable quantities in non-ferrous foundries: in particular, brass contains copper, zinc, and lead; bronze is comprised primarily of copper and tin. Due to the large ratio of ferrous sands to non-ferrous sands, it is possible that the Pennsylvania composite sand samples had low enough heavy metal concentrations that only toxicity from organics was exhibited by the Microtox™ system. When only non-ferrous sands were tested, however, high Microtox™ toxicities likely resulted from metals rather than organic binders or additives. As *Daphnia magna* toxicity was only observed in non-ferrous sand leachate samples, it is possible that these organisms were not sensitive to the organics present in the composite sands but were affected by the metal-associated toxicity of the non-ferrous sands. The reason(s) for the lower Microtox™ toxicity of non-ferrous sands when metal toxicity was eliminated were not clear.

CHAPTER 6

METHODS AND MATERIALS

6.1 INTRODUCTION

This chapter will successively address the following issues: sample site selection, sample procurement, leachate generation, bioassay testing, and organic contaminant testing.

6.2 SAMPLE SITE SELECTION AND PROCUREMENT

The foundries tested during this project were largely those which had been previouslyinvolved with another INDOT study (Javed, 1994) which focused on 'geotechnical' properties and characteristics. Three additional foundries were subsequently included during the courseof the study, both to broaden the range of foundry types and to accommodate site-specific requests.

One- to five-pound samples were collected by foundry or university personnel from a total of thirteen (13) foundries for subsequent testing during this project, as follows:

- Ten (10) ferrous greensand foundries,
- One (1) ferrous 'no-bake' (chemical binder) foundry,
- One (1) steel foundry, and
- One (1) aluminum foundry.

In addition, aged waste sand samples were obtained from the following locations:

- Two (2) ferrous greensand foundries,
- One (1) steel foundry, and
- One (2) aluminum.

Finally, the following virgin materials were also subjected to bioassay testing:

- Thirteen (13) virgin sands,
- Two (2) clays (bentonite),
- One (1) sea coal,
- One (1) shell core sand,
- One (1) cellulose, and

- One (1) fire clay.

The majority of these samples were packed in glass jars, cans, or zipper storage bags and returned to Purdue University for storage at 4°C prior to eventual testing. All samples were labelled with the appropriate information to identify sample location, type, and date.

6.3 LEACHATE GENERATION

Samples were mixed by stirring. From each sample, 20.00 ± 0.05 grams was placed in a flask and 80 ± 1 ml NaCl solution was added. The NaCl was used to simulate the natural environment of the bacteria; a 2% NaCl concentration was used for Microtox™ test samples and 0.5% NaCl was utilized for nitrifier testing. Controls consisted of NaCl solution without sand. Each flask was covered with parafilm, manually agitated to break up clumps, and placed on a shake table for 18 ± 2 hours. The solution was then allowed to settle and 30 to 40 mL of supernatant was poured into polycarbonate centrifuge tubes. The samples were centrifuged for 16 minutes at 10,000 RPM (approximately 10,000 g). The centrifuge supernatants were then filtered through 1.5 µm pore size glass fiber filters. pH was recorded and, when necessary, a phosphate buffer solution was used to adjust pH to between 6.5 and 8.0 for Microtox™ or between 7.5 and 8.0 for nitrifier bioassays. Samples were analyzed immediately or transferred into borosilicate glass vials, covered with parafilm, capped, and stored at 4 °C for no more than 72 hours.

6.4 MICROTOX TESTING PROTOCOL

The Microtox™ 90% Comparison Test, suggested for use with samples of low toxicity, was used to determine foundry sand toxicity. In each test, five leachate replicates were compared with five control replicates consisting of 2% NaCl solution with nothing added. The process can be summarized as follows. Freeze-dried Microtox™ reagent (*Vibrio fischeri*) was reconstituted and, in each of ten cuvettes, the light produced by 0.1 mL of the reagent was measured. Then, 0.9 mL sample was added to five cuvettes and 0.9 mL control diluent was added to the other five cuvettes. Light output from each cuvette after five and fifteen minutes was measured, and the percent difference between initial light output and final light output was quantified. The replicate values wereaveraged and an overall toxicity value and range of certainty were calculated.

For quality control purposes, complementary bioassay tests were conducted on an approximately monthly basis using reference toxicants. A known organic toxicant (10 mg/L phenol) was used for this purpose, thereby verifying the repetitive sensitivity of the employed Microtox™ cultures.

6.5 NITROTOX TESTING PROTOCOL

Nitrifier bioassay testing was conducted with three replicates for each sample. Stock nitrifying

solution, cultivated as described by Alleman (1986) and having a concentration of 3,000 to 3,500 mg/L, was aerated for 45 minutes to remove any residual ammonia. After allowing the solution to settle for approximately 20 minutes, 80% of the supernatant was decanted, ammonia was added to a concentration of 33 mg/L as ammonia. This thickened solution was aerated for five minutes.

Polycarbonate centrifuge tubes were filled with 10 mL sample, 2.5 mL bacterial solution, and 0.6 mL 1000 mg/L NH_4^+-N. Control solutions consisted of 0.5% NaCl solution in place of foundry sand leachate. The mixture was rotated end over end for 20 minutes, after which 200 µL of 5000 mg/L MTT (98% powder; Aldrich Chemical 13,503-8) solution was added to each tube. This was rotated for 15 minutes and then centrifuged at 10,000 rpm for 10 minutes. Eight mL of centrifuge supernatant was removed and 8 mL isopropyl alcohol to solubilize the MTT-formazan crystals. Each tube was shaken to resuspend the pellet and rotated five minutes. The solution was centrifuged for 7 minutes at 10,000 rpm, and the absorbence of the supernatant at 570 nm was measured using a Molecular Devices Vmax^R Kinetic Microplate Reader plate reader, with a reference wavelength of 690 nm. Absorbence was compared with controls.

6.6 GAS CHROMATOGRAPHIC/MASS-SPECTROPHOTOMETER EVALUATION PROTOCOL

Gas chromatograph/mass spectrophotometer studies were performed (i.e., in conjunction with analytical assistance provided Purdue University's Mass Spectrometry Service) on two types of samples obtained from the tested sands, including bothleachate and off-gas forms. A total of four (4) sands were subjected to this GC/MS testing effort, including three (3) waste sands (obtained from foundry locations F1, F9, and F11) and one virgin sand.

The tested leachates were produced using the same 4:1 water:solid ratio as was used with the bioassay tests. However, given the potential for salt-related analytical interferences with the GC/MS instrumentation, the saline leachant was replaced with deionized water.

Off-gas samples were obtained from these sands by passing clean (i.e., prefiltered using activated carbon) compressed air in an up-flow fashion through a ~200 gm sample, with off-gas contaminants then being adsorbed onto downstream thermal desorption tubes (Carbotrap^{TM} 300, Supelco, Inc.). Following 20 minutes of air purging at a rate of 100 ml/min, these tubes were capped and stored for subsequent thermal desorption. Thermal desorption of the Carbotrap^{TM} tubes was done on a Dynatherm Model 851 thermal desorption unit. The samples were desorbed for 2 minutes at 320°C onto a DBI, 30 m X 0.25 mm capillary column. The column was temperature programmed from 50 °C for 0.1 minute to 280 °C at 15 °C/minute. Electron impact mass spectral data was collected on a Finnigan 4000 mass spectrometer at 70 eV, scanning from 41 to 400 AMU.

CHAPTER 7

RESULTS AND DISCUSSION

7.1 INTRODUCTION

Data were obtained for thirteen virgin sandsamples and for samples from eleven gray and ductile iron foundries, one steelfoundry, and one aluminum foundry. Measurements included leachate pH values, 5- and 15-minute Microtox™ response data, Nitrotox response data, and, for four samples, preliminary identification of organic contaminants. Microtox™ testing consisted of extraction controls and standard testing. Additionally, a summary of chemical-specific waste characterization performed by one of the foundries over a period of twelve years has been included.

7.2 pH

Prior to bioassay analysis, the pH of each leachate was tested and, if necessary, adjusted to a value appropriate for bioassay testing. Virgin sand pH values averaged approximately 6.85, being slightly acidic. Ferrous greensand WFS leachates were usually slightly basic, although pH levels ranged from 6.5 to 10.1. The chemically bound WFS leachates had neutral pH levels, ranging from 6.8 to 7.3. Leachates from aluminum foundry waste sand sample leachates were slightly basic. Steel foundry waste sand pH levels were not measured. No apparent correlation existed between initial pH and bioassay response.

7.3 MICROTOX

7.3.1 Overview

Although the commercial name, Microtox,™ inherently implies that 'toxicity' is being evaluated, the relative meaning of any such 'toxic' indication is subject to considerable interpretation. All of the tested sands during this project had, in fact, already been proven to be 'non-toxic' (by a considerable margin) according to the applicable regulatory criteria.

The involved concept of using a Microtox™ test to evaluate these foundry sand leachates, therefore, is moreso focused on qualifying a bioassay response relative to virgin materials. For those samples which fall within the response range statistically established for clean, natural sands, their Microtox™ behavior provides a strong indication that these residuals are suitable for subsequent reuse. Conversely, for those sands with which their Microtox™ response shows excessive negative impacts (i.e., beyond clean, natural sands), these results would presently warrant excluding these sands from further consideration for beneficial reuse. Simply put, the Microtox™ bioassay will provide another quantifiable layer of validation to the claim that ferrous foundry sands are *"cleaner than dirt."*

The following presentation of the bioassay results consequently hinges on an evaluation of 'negative responses,' as opposed to toxicity. In many instances, the tested sands showed little if any indication of a negative Microtox™ response. However, for a limited group of foundry sands, some of these results repeatedly demonstrated a 'negative response' whose distinct difference from the natural sands would presently preclude their constructive reuse. The underlying point to be made is that the Microtox™ test is not being used as a definitive calibration of toxicity, but to identify and 'fingerprint' those sands whose quantifiable character appears commensurate with that of natural materials (i.e., perhaps not "cleaner than dirt," but effectively indistinguishable)!

Figure 3 displays an overall summary of the 5-minute Microtox™ response levels observed with the virgin sands and all thirteen foundries from which samples were obtained. Bioassay response (i.e., depicted on the y-axis) is quantified as a percentile decrease in light output for test microorganisms exposed to sand leachates as compared to those exposed solely to a specially prepared 'control' water. Each data point depicts the mean response for all samples from the sand type it respectively represents. The range of response values from each sample type is shown by the vertical bars passing through the data points.

As virgin sands are the most appropriate standard to which WFS can be compared, a solid horizontal line is used to represent the mean response of the virgin sands tested. The dotted horizontal lines indicate one standard deviation above and below the mean response of virgin sands.

In Figure 4, 15-minute Microtox™ results are presented. It is seen that the mean 15-minute responses were very similar to 5-minute results. This is important as it suggests that the observed light inhibition was largely due to released organics rather than metals.

7.3.2 Raw Materials

While the following discussion will address the results observed with the virgin sand tests, an attempt was also made to run bioassays on a number of additional 'virgin' materials, including: fire clay, bentonite clay, and cellulose. However, these products were not amenable to producing testable leachates since these materials swelled to such an extent that they consumed all of the added test water. While tests completed on virgin sea coal showed no negative impact, fresh shell core sand completely inhibited light production. By inference, chemicals released from this shell core sand were extremely deleterious to the Microtox™ microorganisms. Apparently, though, these latter contaminants were being chemically and thermally transformed during the core making and casting processes since the post-casting bioassay results did not demonstrate any such residual impact (see related discussion in following sections).

Figure 5 contains Microtox™ data for thirteen (13) virgin sand samples. In this and all subsequent

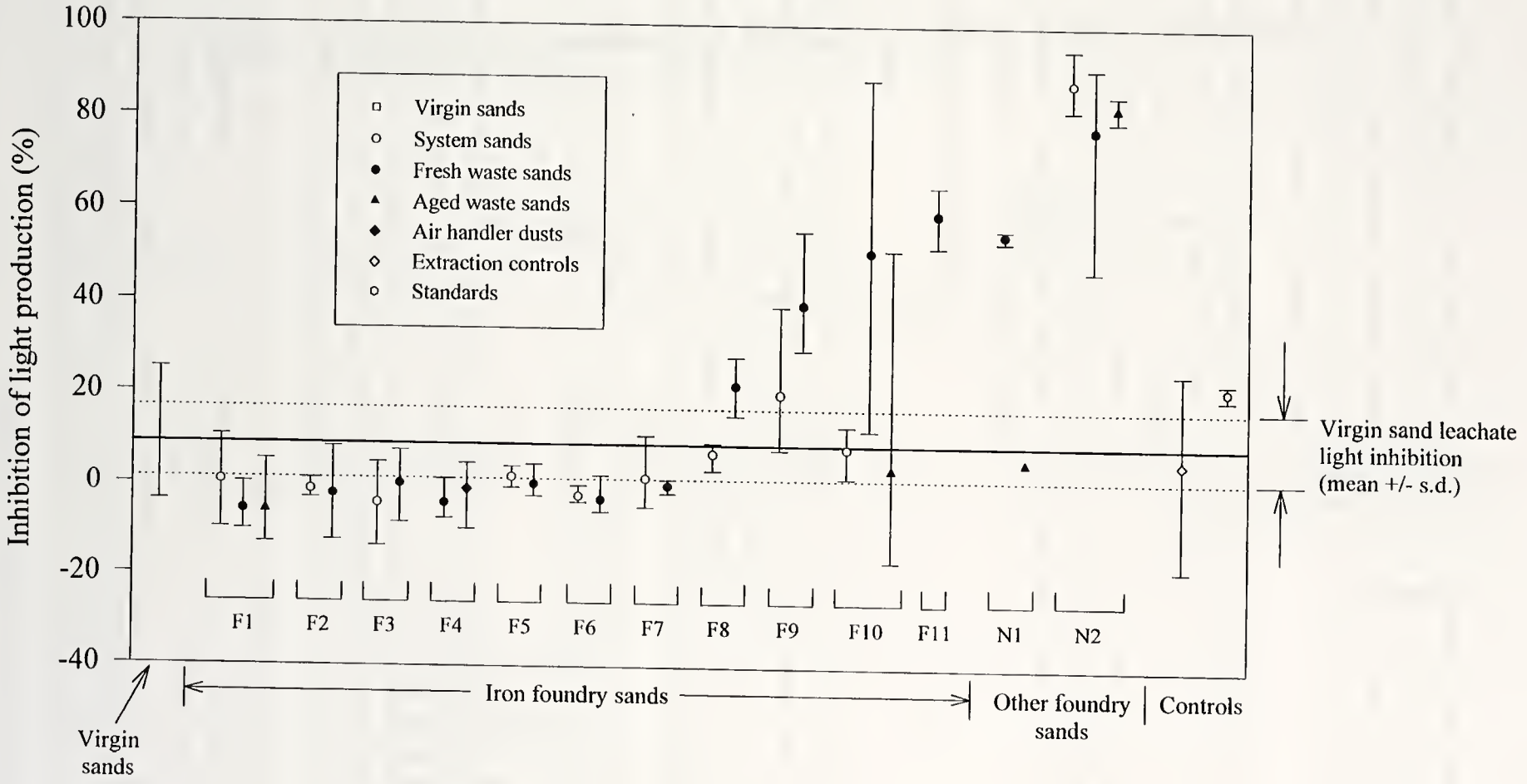


Figure 3: Microtox™ Response to Foundry Residuals After 5 Minutes

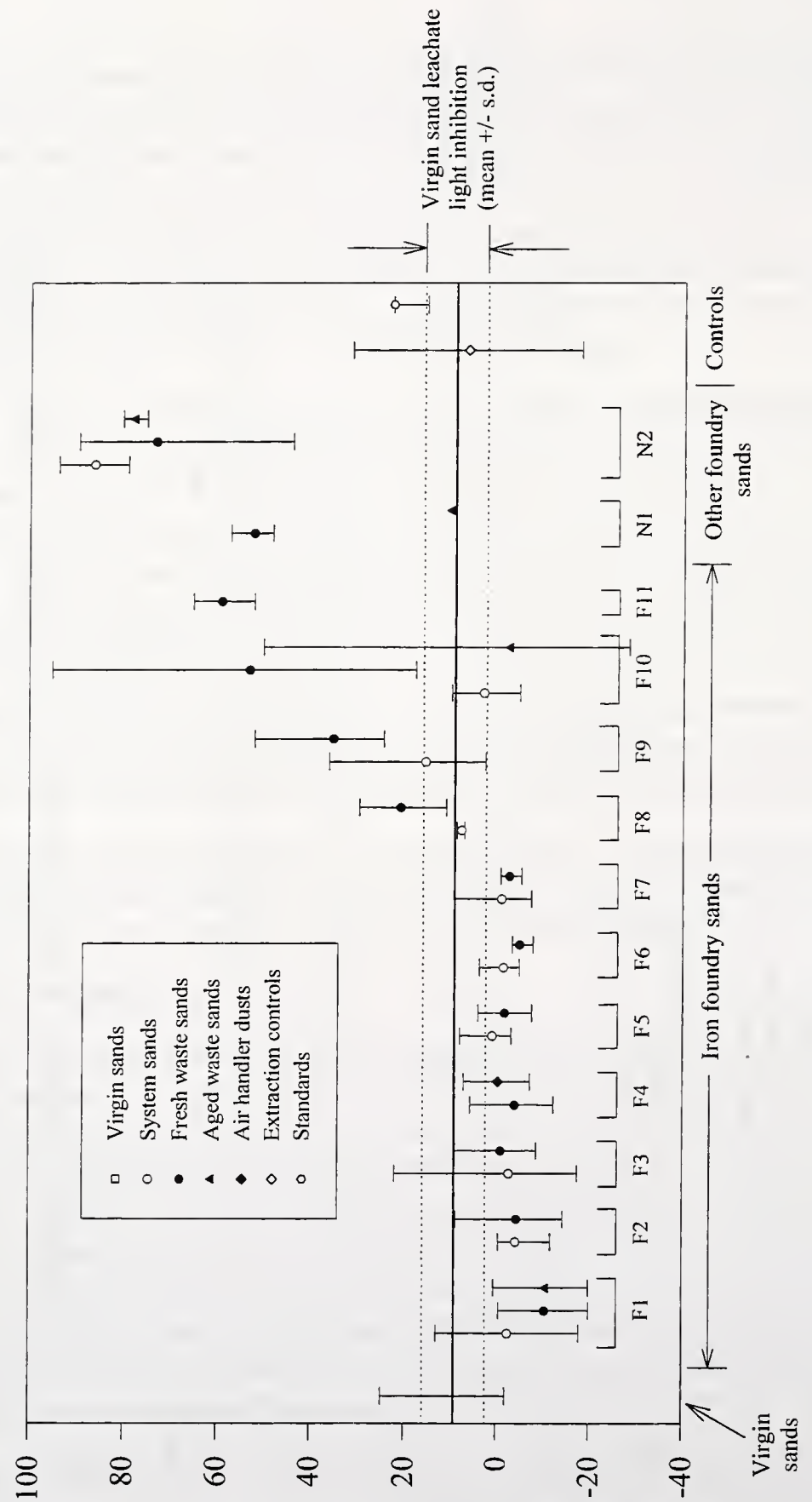


Figure 4: Microtox™ Response to Foundry Residuals After 15 Minutes

Microtox™ response figures, each data point represents the response of one sample, and error bars show the estimated error of each measurement. The samples with the highest and lowest response, numbers 1 & 2, were retested to assure correct readings. For the thirteen samples, mean inhibition of light production by virgin sand leachates was 9.0 and 9.15% for 5- and 15-minute readings, respectively, with standard deviations of 7.7 and 6.85%.

Here again, these latter percentile response levels are relative to a 'clean' control water whose known composition does not exert a negative impact on the employed bacteria. By comparison, the virgin sand leachates engendered a range of bioassay effects which on average were marginally inhibitory (i.e., reducing light production due to an unknown stress). While the magnitude of this impact is not at all extreme, there is no readily obvious reason why the virgin sands should behave in this fashion. The fact remains, though, that these virgin sand results qualify as the best natural benchmark against which the foundry sands can directly be judged.

7.3.3 Ferrous Foundry Operations

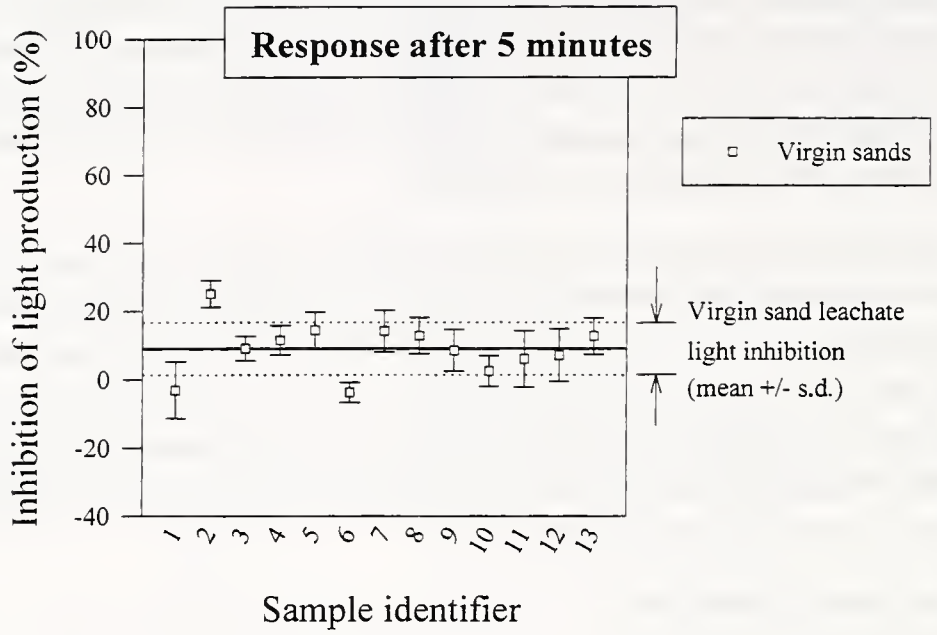
7.3.3.1 Foundry F1

Foundry F1 was a large gray iron foundry, casting approximately 1,000 tons metal per day in castings ranging from 1 to 70 pounds in weight. During the period of sampling associated with this study, the 'F1' foundry used approximately 125 to 150 tons of new sand per day and a phenolic urethane cold-box compound as the primary core binder. Approximately 25 additional tons of shell core sand were also used each day. Figures 6 and 7 display system and fresh waste sand Microtox™ response.

Out of nine (9) system sand samples, only one had a negative response greater than the virgin sand average. In addition, another nine (9) fresh waste sands had bioassay results which were consistently below the virgin sand average.

The bioassay results observed with nineteen (19) aged waste sands are shown in Figure 8. Foundry F1 was unusual in that it owned and operated a monofill rather than having to send its WFS to a municipal landfill. Aged waste sands from the monofill were sampled over time, including a collection of ten samples on one day. Aged waste sand responses followed the same trend as the rest of the sands from this foundry, falling well below the virgin sand level.

The bioassay response to fresh and aged waste sand leachates was lower than that observed with the system sand leachates. The process of in-house recycling of waste sands includes cooling, removing pieces of metal, fines, and core butts, and adding clay, water, and other organic additives. It is possible that there was anorganic additive or clay which caused inhibition of the Microtox™ organisms and which was removed through the casting process. This effect was so small, however, as to be unimportant with respect to the overall bioassay results. By comparison, as will be described



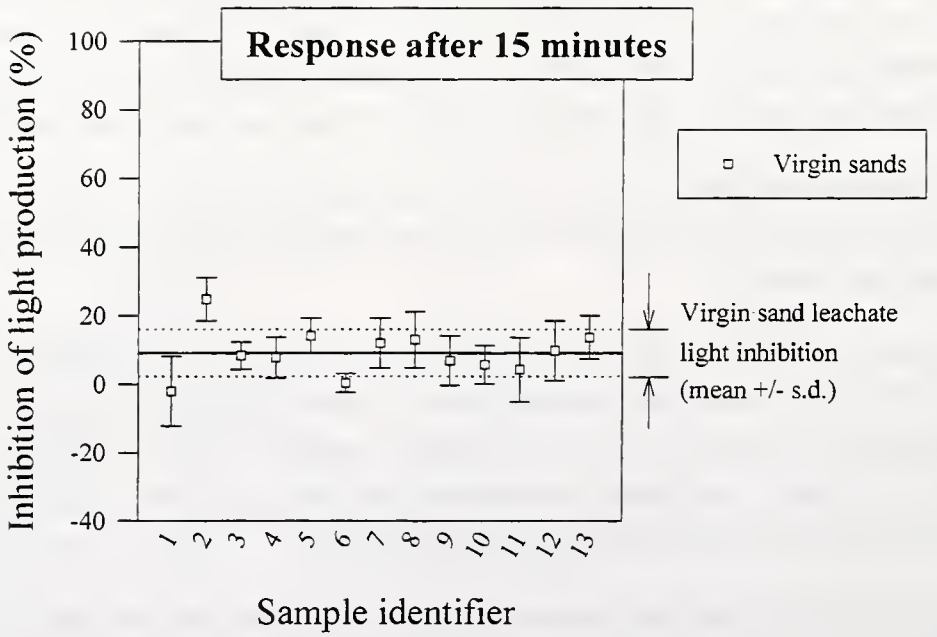
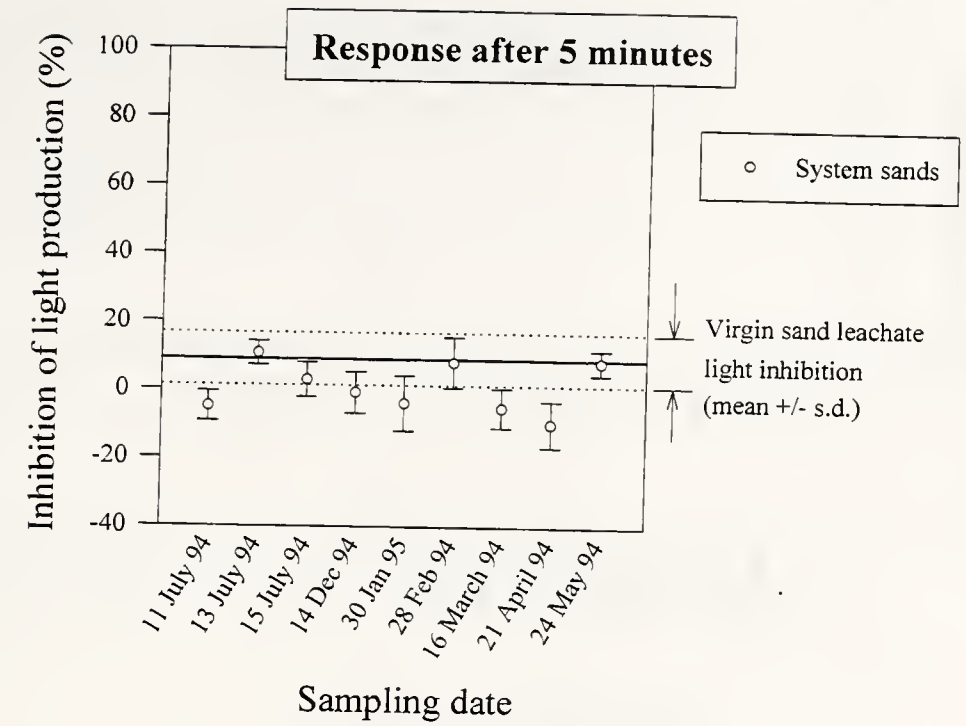


Figure 5: Microtox™ Response to Virgin Sands



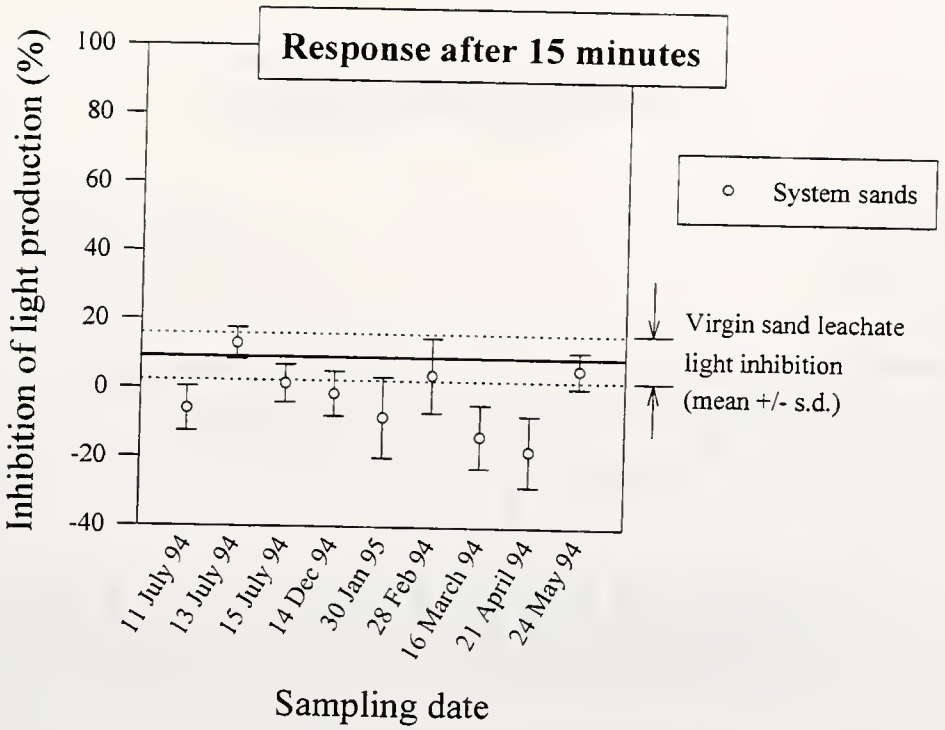
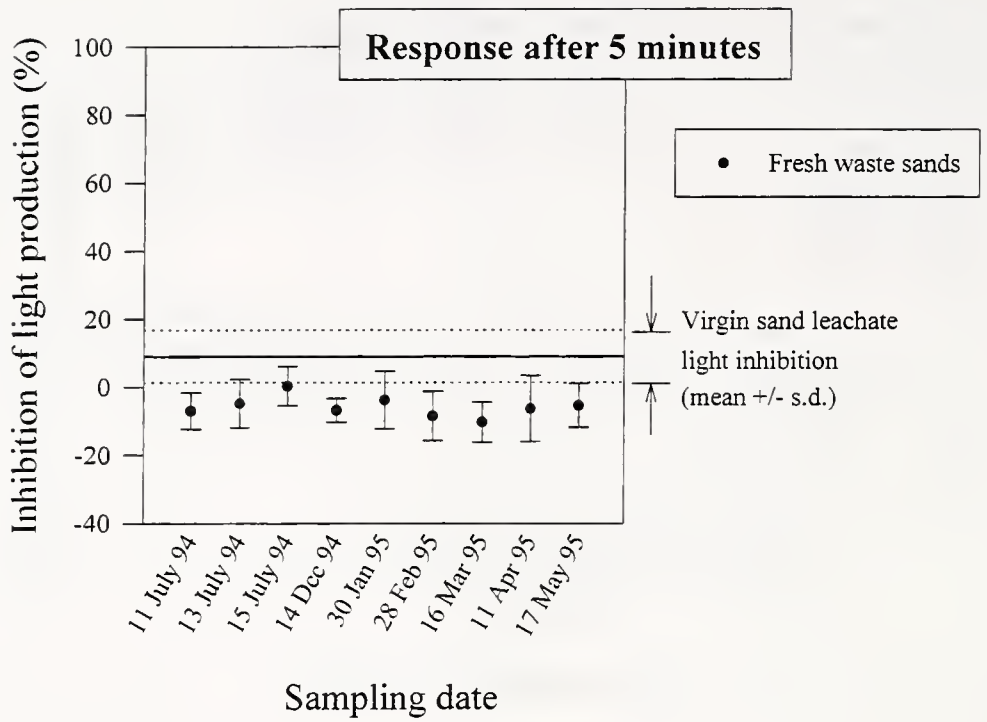


Figure 6: Microtox™ Response to Foundry F1 System Sands



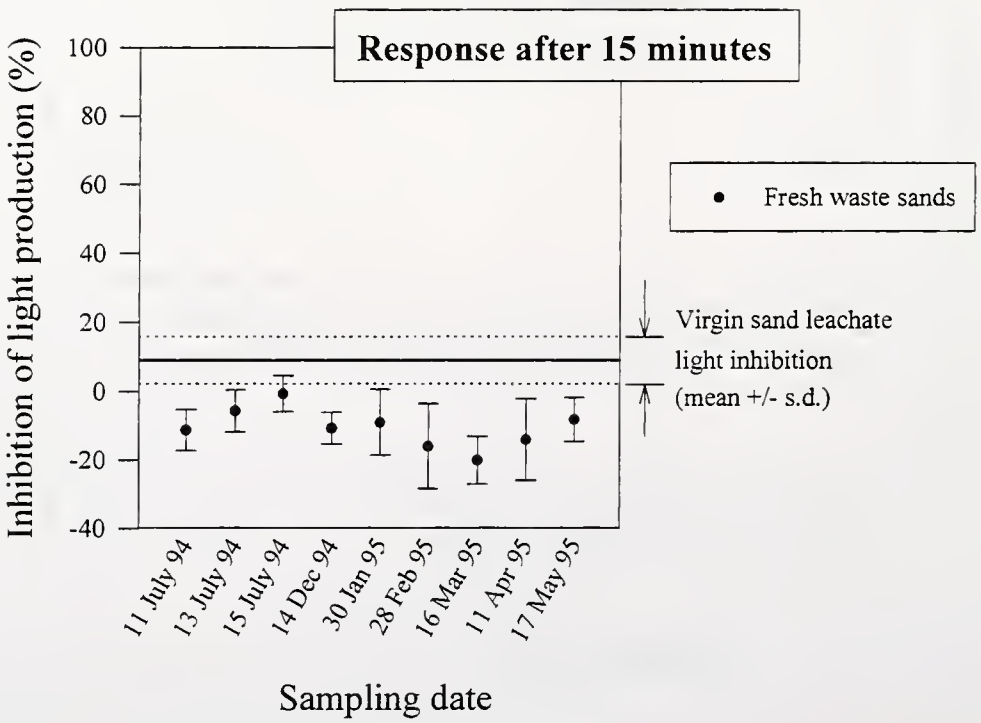
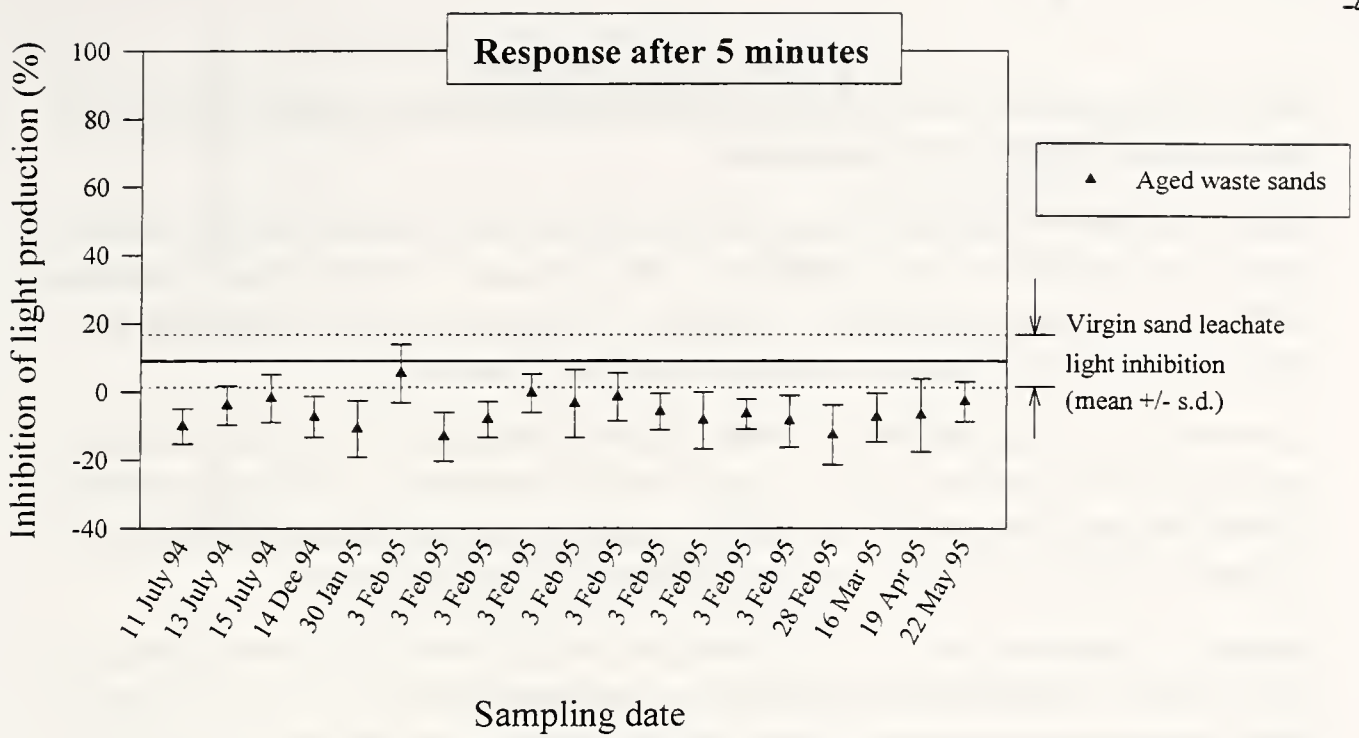


Figure 7: Microtox™ Response to Foundry F1 Fresh Waste Sands



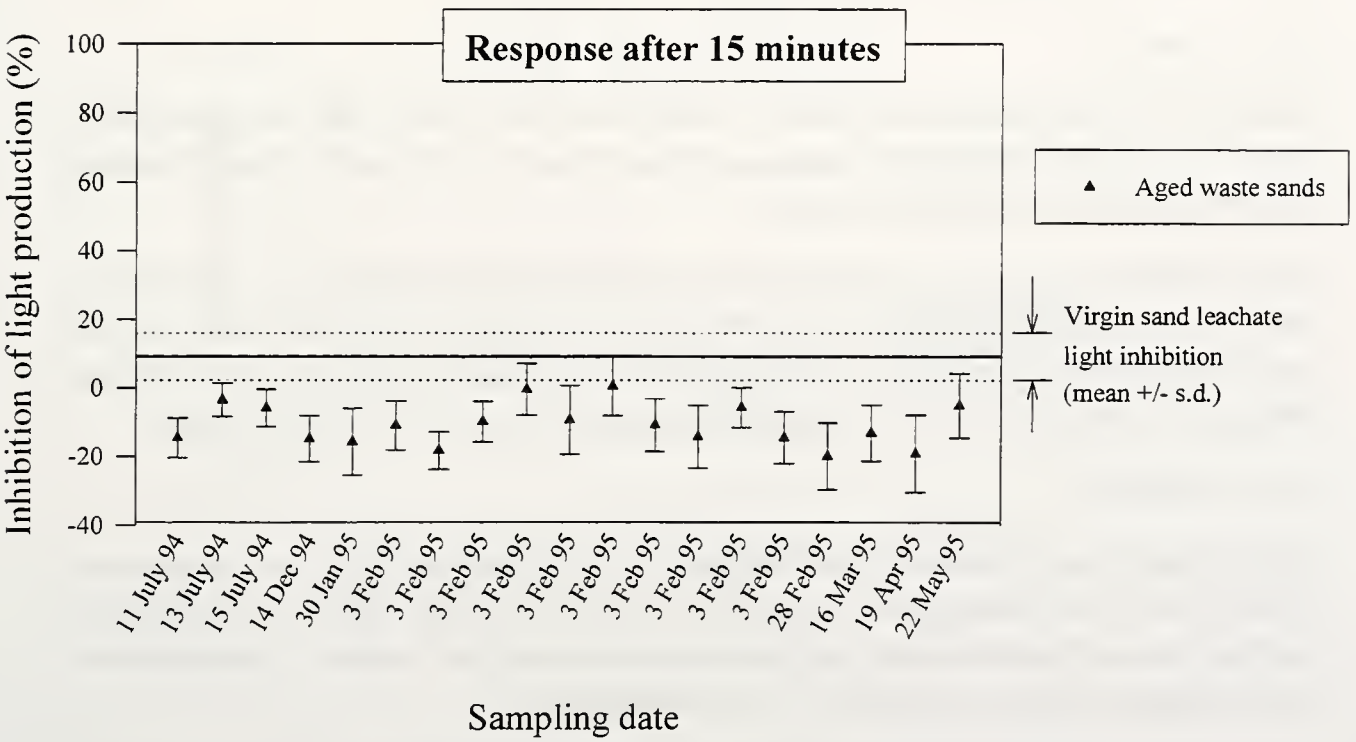


Figure 8: Microtox™ Response to Foundry F1 Aged Waste Sands

later, the waste sands tested at some of the other foundries exhibited bioassay responses greater than those measured with their system sand samples.

In short, there was no indication of negative bioassay response with these sands, and there were no chronological aberrations in this qualification. This conclusion is complemented by historical documentation on 'metal' TCLP behavior compiled by this foundry (provided as confidential data), which repeatedly showed little if any problem with leachate contaminants.

According to this foundry's most recent 'metallic' TCLP characterization study, barium was the only parameter which fell between Indiana's Type III and IV classification. Based on the 'Neutral Leachate Procedure,' this foundry's waste sand also exhibited a tendency to towards elevated levels of fluoride and pH, but here again these values were below the Type III criteria.

Although no analogous data (i.e., TCLP results, etc.) was provided by any other foundry, the impression given by regional foundry professionals was that these fluoride and pH excursions beyond Type IV criteria were not uncommon. Indeed, their expectation was that the ferrous foundry sands would readily meet the other Type III (if not Type IV) parameters. The potential exceptions to this qualitative judgement would likely involve iron and manganese, for which the relevant concerns would beaesthetic as opposed to health related.

7.3.3.2 Foundry F2

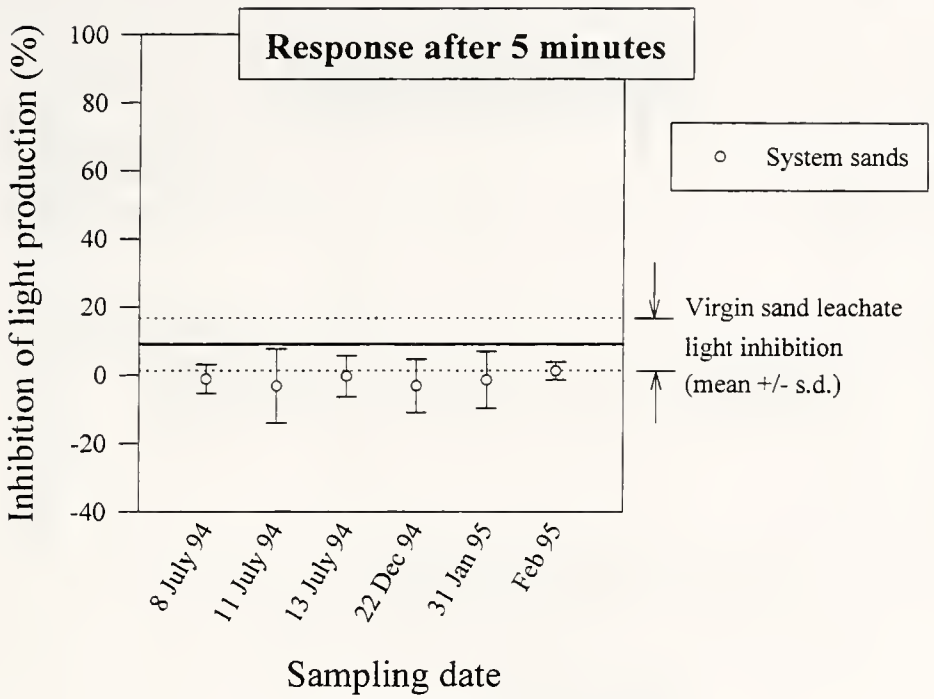
Foundry F2 was a smaller gray iron foundry. Average metal cast and sand used was approximately 95 and 18 tons per day, respectively. Casting sizes ranged from 1/2 to 50 pounds. Phenolic urethane cold-box and shell core binders were used.

As seen in Figures 9 and 10, all system and fresh waste sands displayed a Microtox™ response at or below the virgin sand response level. Response to fresh waste sand leachates seemed to vary more than those to system sand leachates, and also seemed to increase between December 1994 and February of 1995, but there were not enough datato determine whether a real trend existed.

7.3.3.3 Foundry F3

Another small foundry, Foundry F3 cast gray iron at a rate of 50tons per day. Sand usage per ton of metal was ~20 to 25 tons per day. Approximately 85% of the cores were bound with phenolic urethane cold-box binders, although shell core and oilsands were also utilized. Casting weights at the 'F3' foundry typically ranged between 1 and 100 pounds.

Figures 11 and 12 show that with one notable exception, all system and fresh waste sand samples had responses at or below the virgin sandaverage level. No pattern of variation with time was seen.



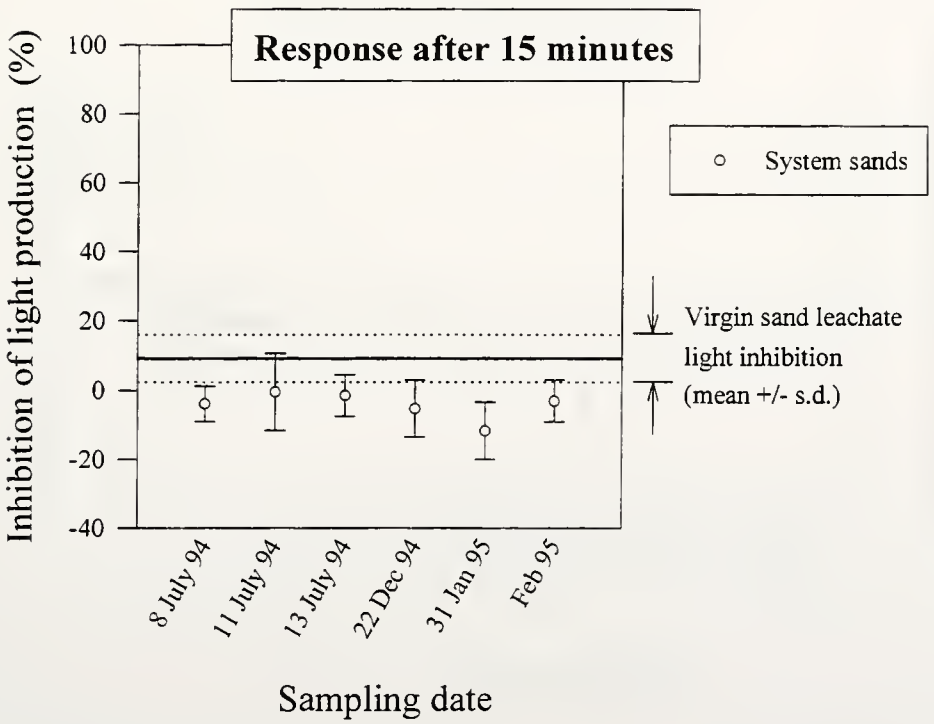
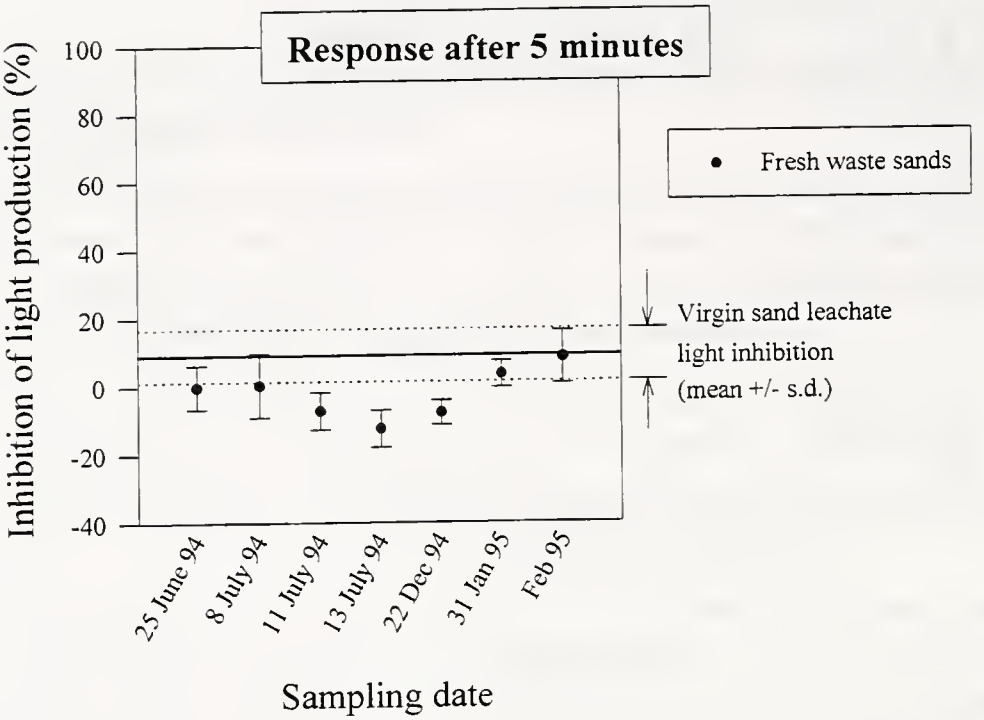


Figure 9: Microtox™ Response to Foundry F2 System Sands



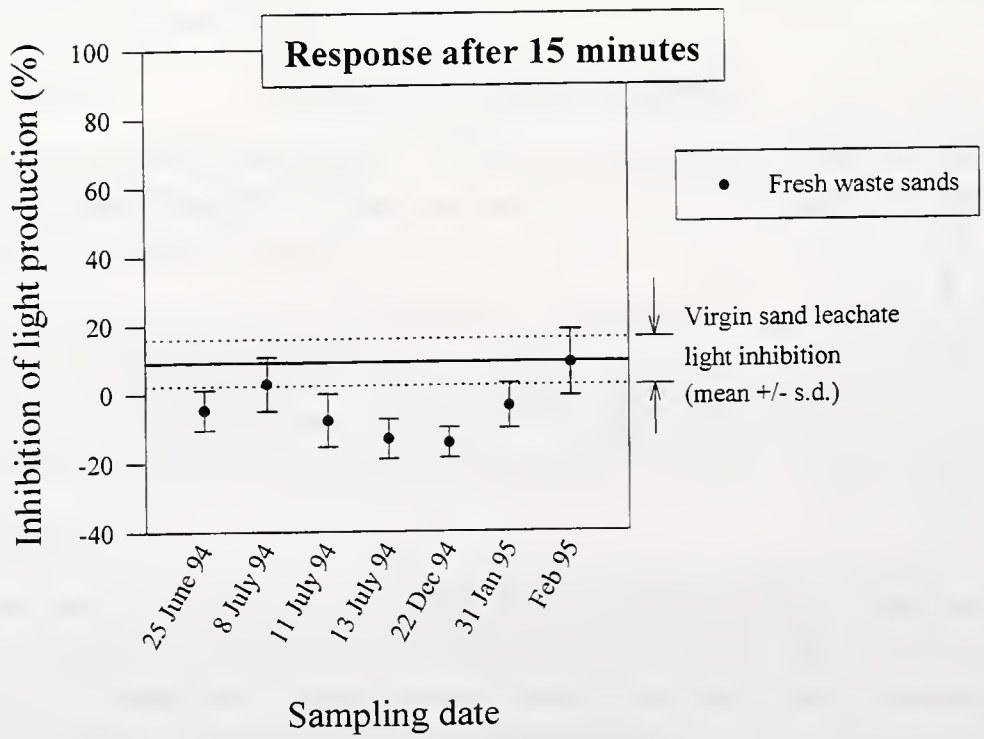


Figure 10: Microtox^{TM} Response to Foundry F2 Fresh Waste Sands

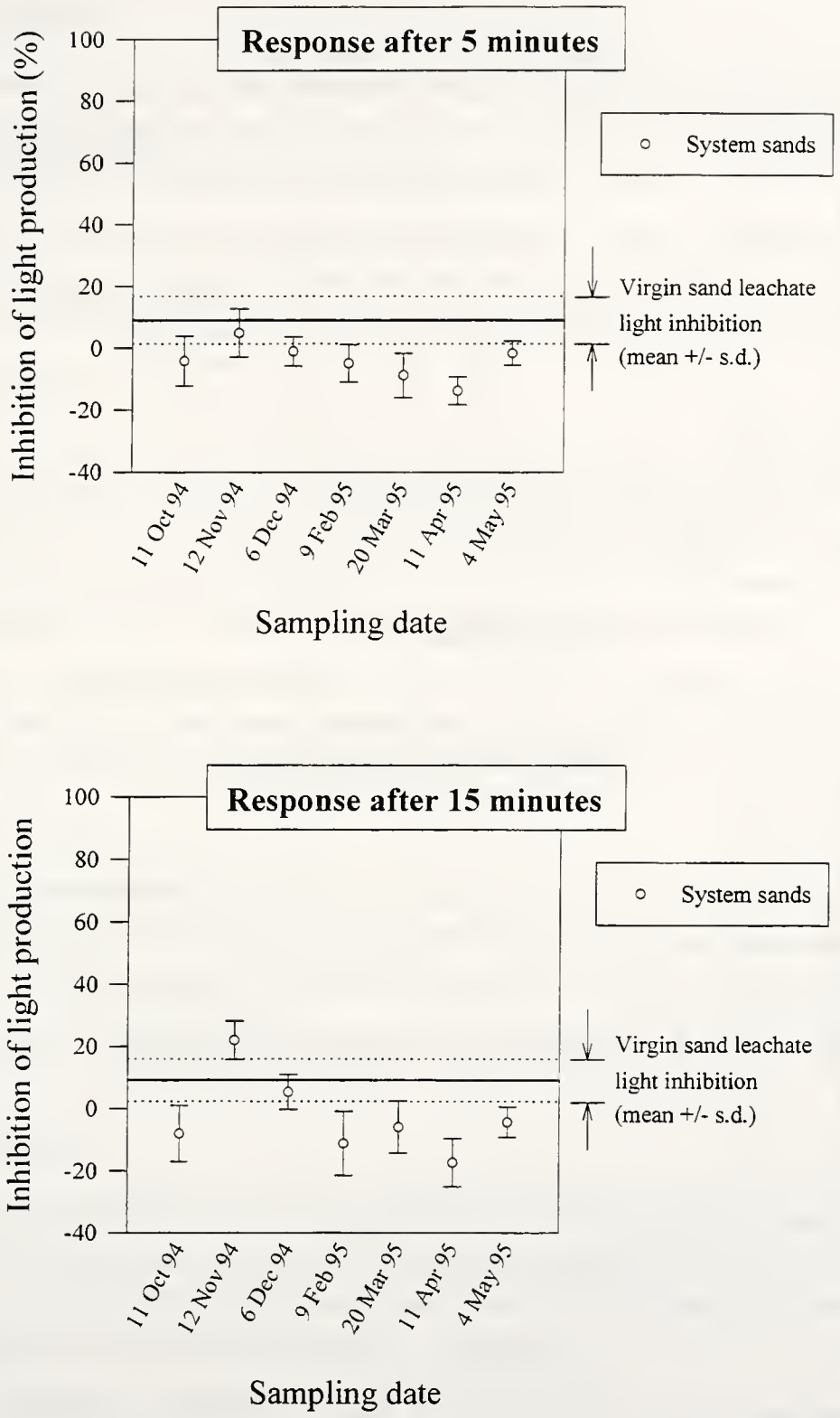
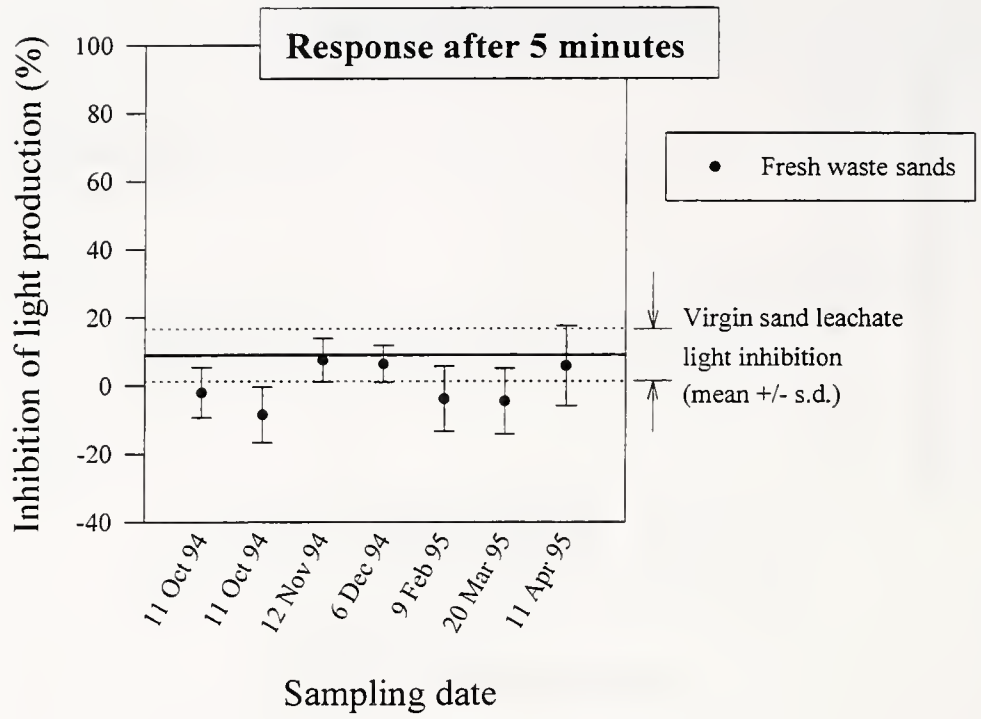


Figure 11: Microtox™ Response to Foundry F3 System Sands



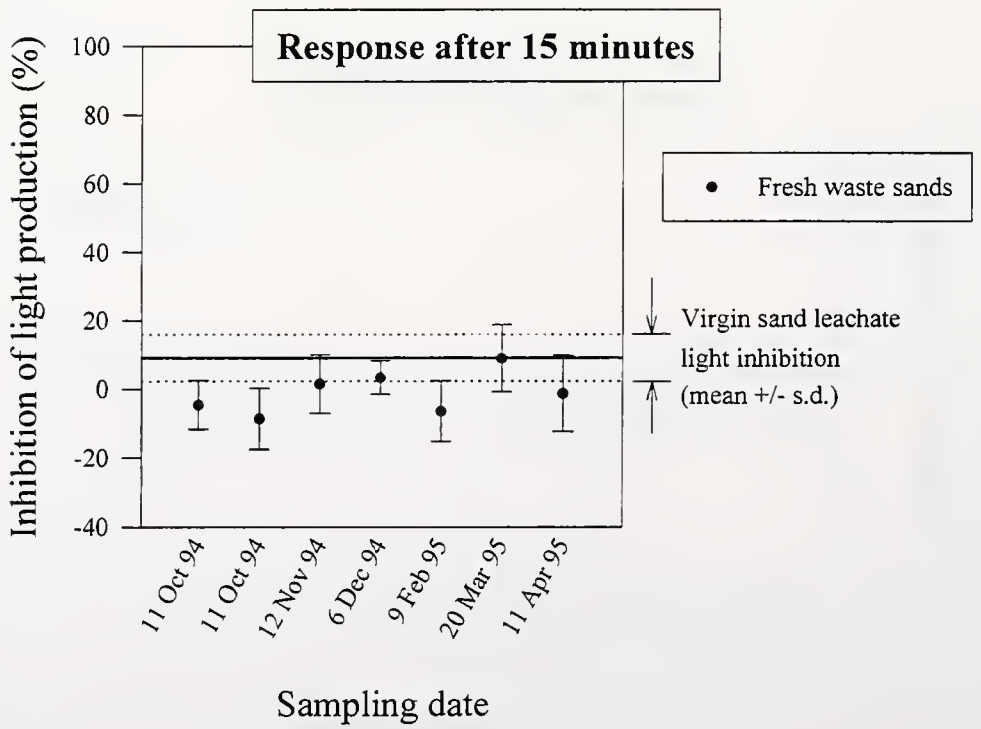


Figure 12: Microtox™ Response to Foundry F3 Fresh Waste Sands

7.3.3.4 Foundry F4

Foundry F4 was a larger gray and ductile iron foundry, casting an average of 350 tons per day. Phenolic urethane cold-box binders were commonly used. Roughly 100 tons of new sand were used each day. Casting weights typically ranged between 5 and 30 pounds.

As Figures 13 shows, all fresh waste sand responses fellbelow that of virgin sands. As shown in Figure 14, response to air handler dust samples, not measured for other foundries, was lower than that of the virgin sands. Neither sample type caused notable variations in light production over time.

7.3.3.5 Foundry F5

Foundry F5 was a gray and ductile iron foundry, producing castings of sizesfrom ounces to 3,000 pounds. Approximately 20 tons of metal were melted each day; two tons of sand were added each day, with 75% as new mold sand and 25% as cores. Of the cores, 5% usedshell core binders, 45% were made with oil binders, and 50% were bound with SO_2 binders. Fewer samples were collected from Foundries F5, F6, and F7, sodata has been presented on only one figure each.

No conclusions regarding time variation can be made. Figure 15 shows that system and freshwaste sands from Foundry F5 all displayed responses below the virgin sand average level. No difference between system and fresh waste sands was observed.

7.3.3.6 Foundry F6

Foundry F6 was a gray and ductile iron foundry casting 50 tons of metal and using 7 tons of sand per day. A phenolic urethane cold-box binder was used for 95%of the cores, with an oil sand utilized for the other 5%. Castings averaged 5.5 pounds with a range of 2 ounces to about 60 pounds.

As seen in Figure 16, all samples from Foundry F6 caused only low levels of inhibition of light production.

7.3.3.7 Foundry F7

Foundry F7 was a smaller gray and ductile iron foundry, casting 30 to 40 tons of metal per day and using approximately 20 tons of sand per day. Casting sizes ranged from 30 to 250 pounds. Sixty percent of their cores were produced using shell binders; the remaining 40% were split evenly between phenolic urethane cold-box and air set.

Microtox™ response is displayed in Figure 17. One sample caused a response at a level approximately equal to the virgin sand average; all other samples caused responses well below this level.

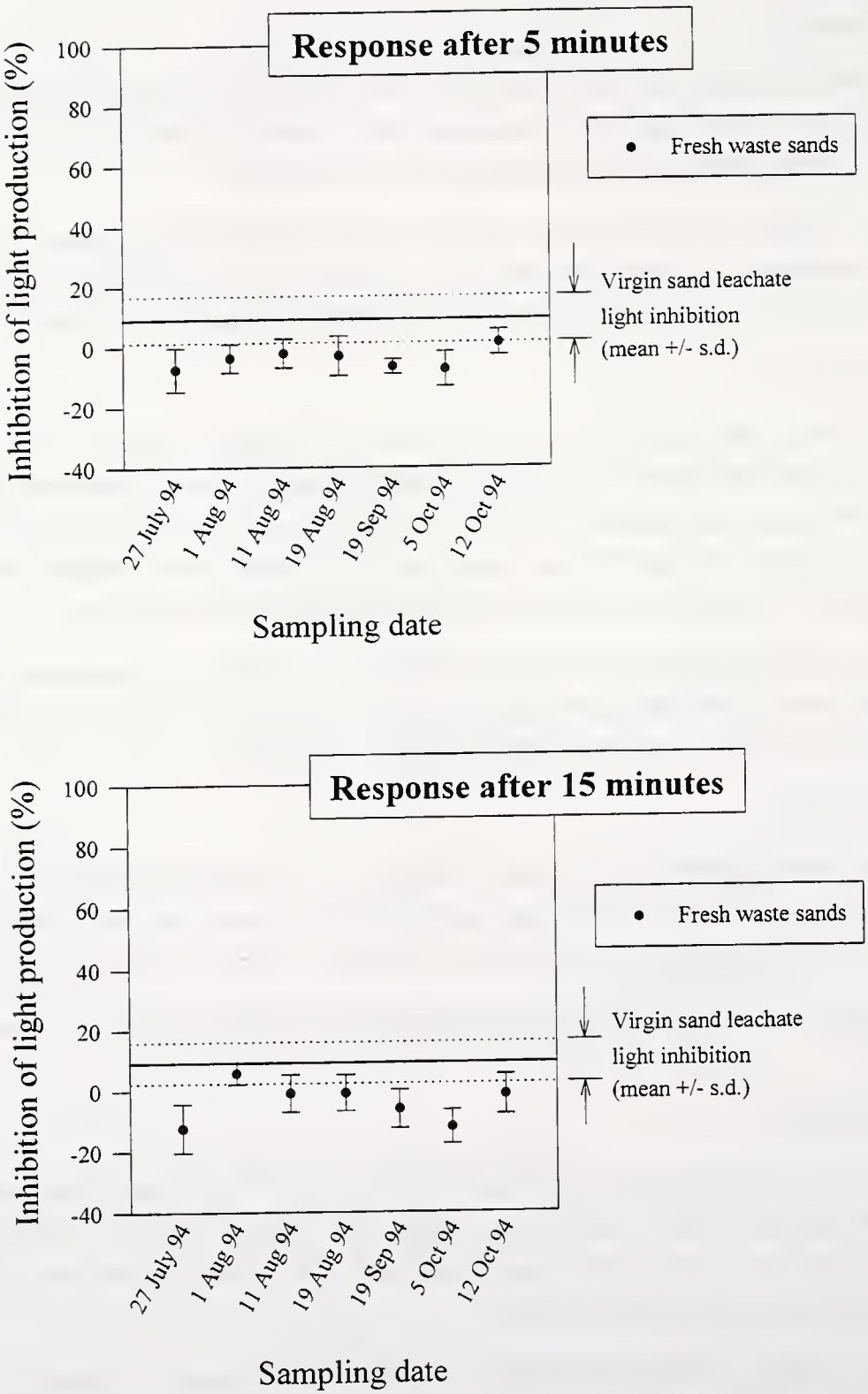


Figure 13: Microtox™ Response to Foundry F4 Fresh Waste Sands

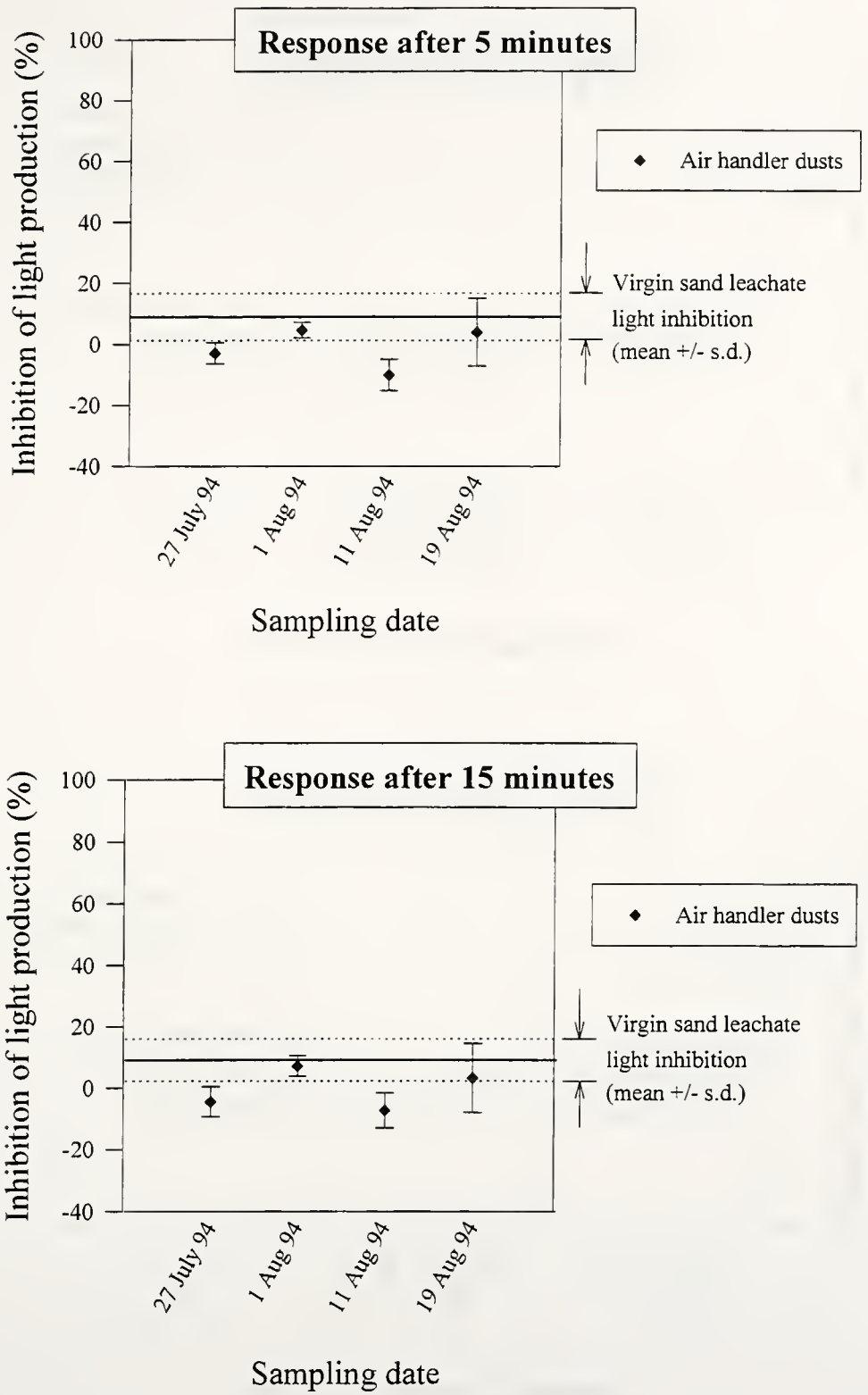
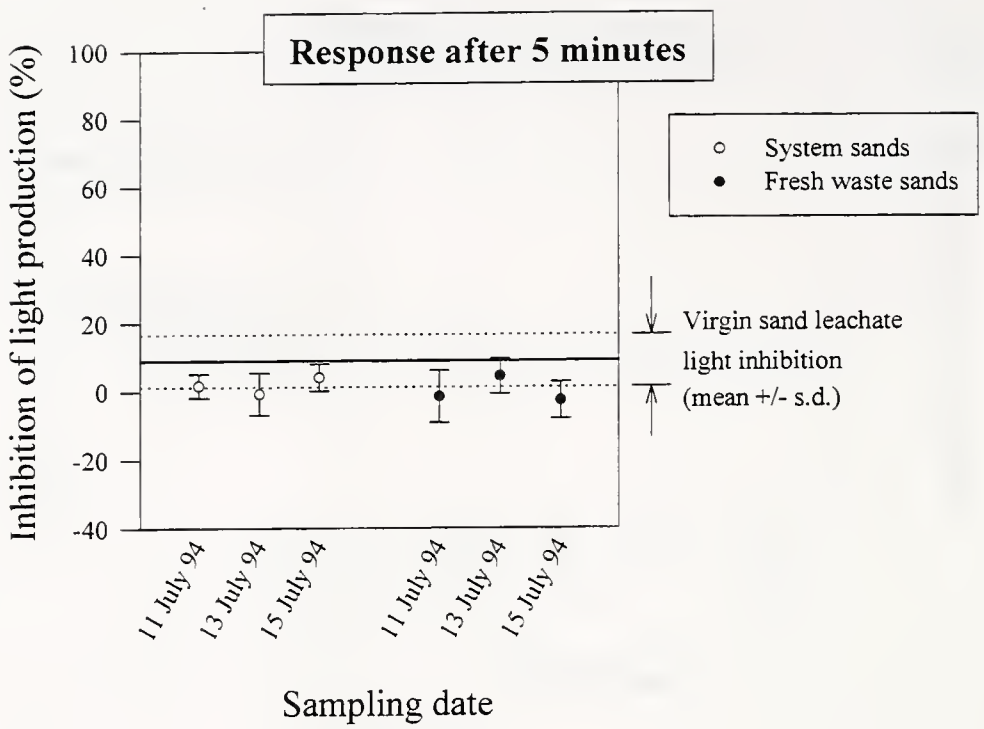


Figure 14: Microtox™ Response to Foundry F4 Air Handler Dusts



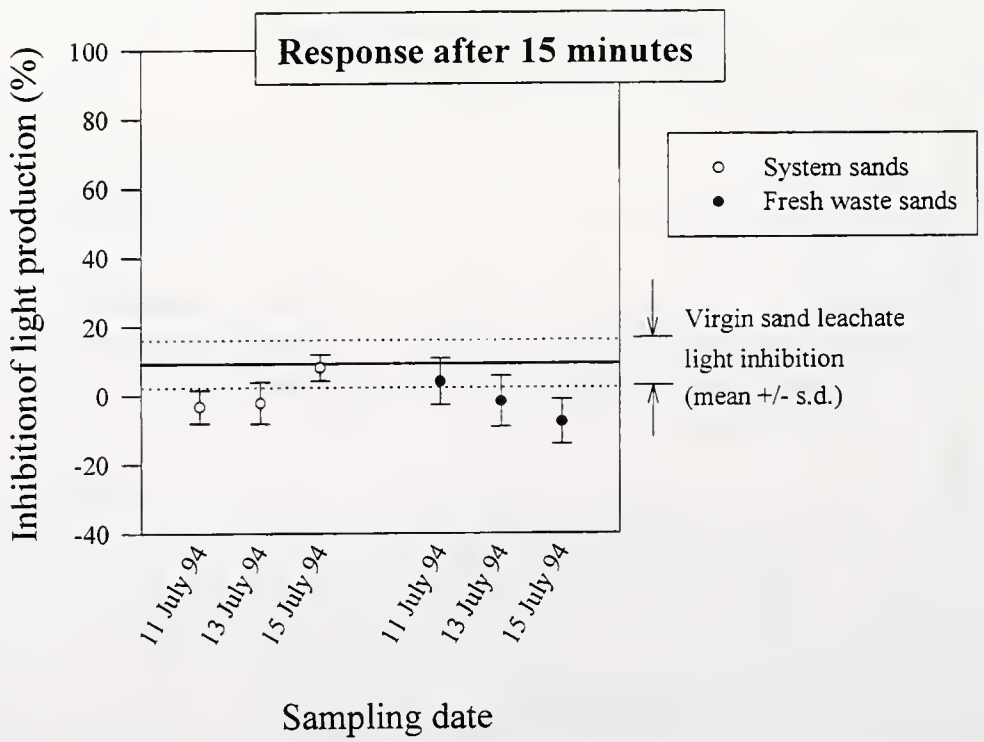
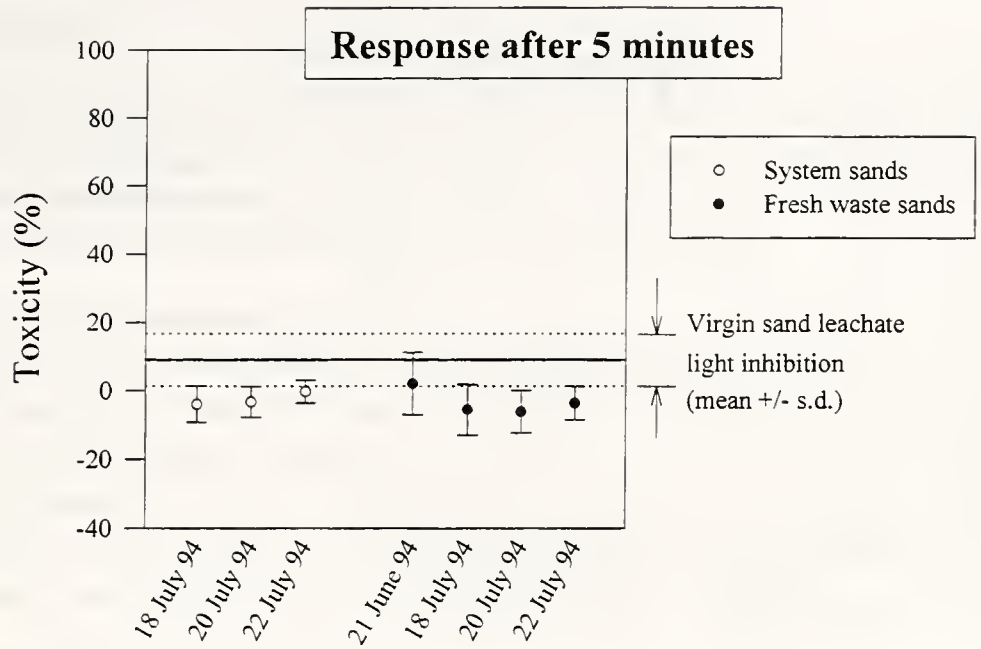


Figure 15: Microtox™ Response to Foundry F5 Sands



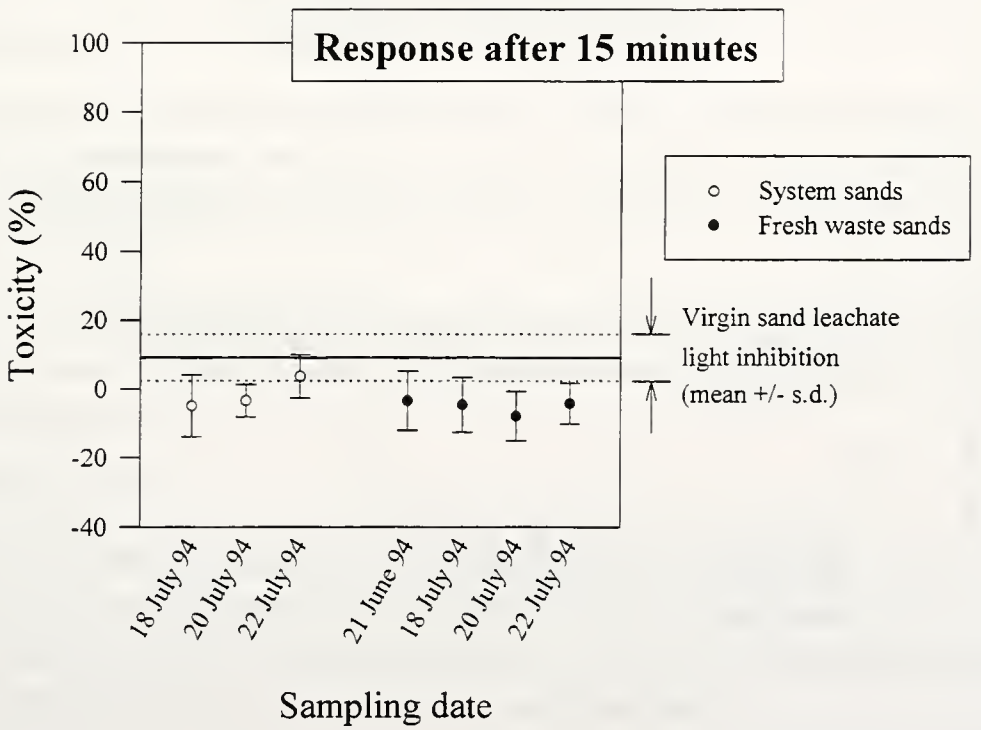
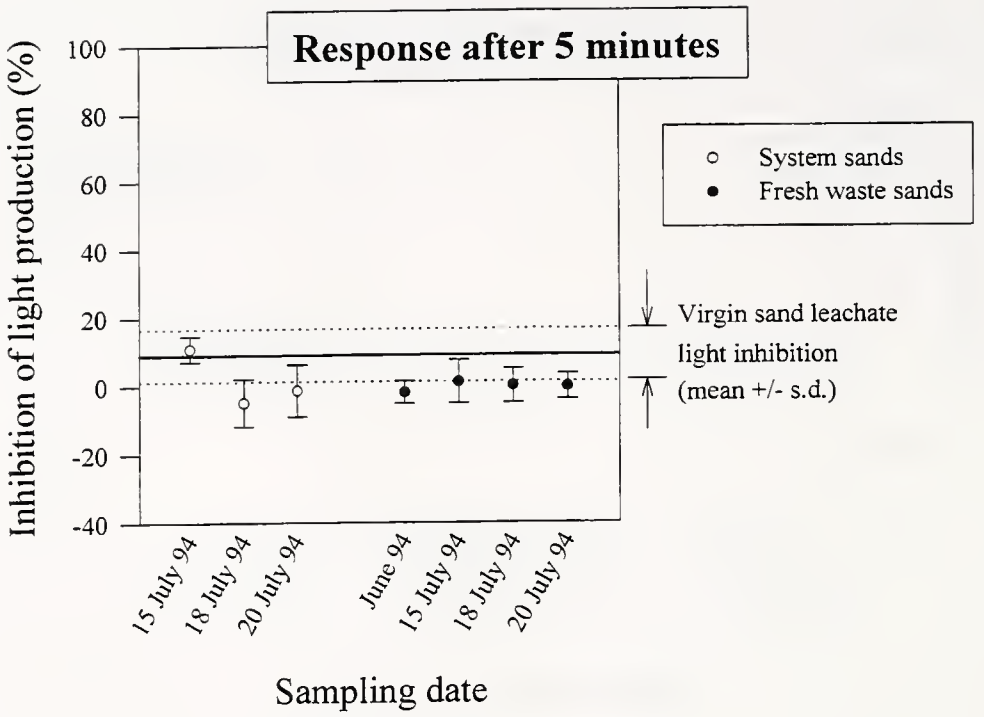


Figure 16: Microtox™ Response to Foundry F6 Sands



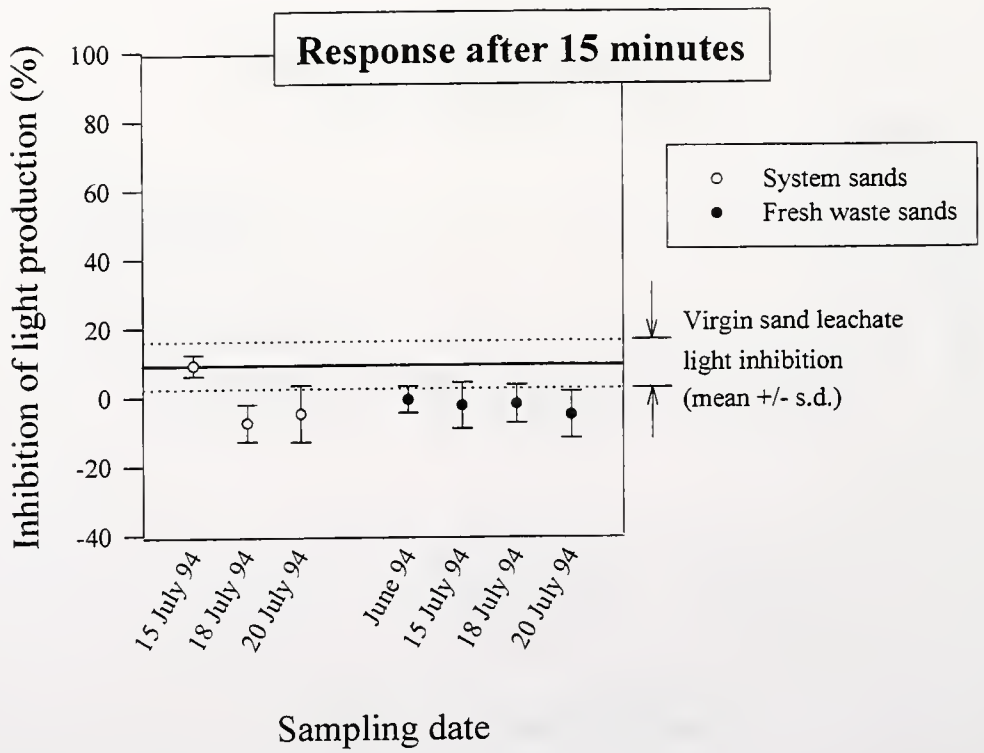


Figure 17: Microtox™ Response to Foundry F7 Sands

7.3.3.8 Foundry F8

Foundry F8 was a gray iron foundry. Daily casting weights were in the area of 700 tons, with 200 tons per day of sand being consumed. Three-quarters of this foundry's cores were produced with a phenolic urethane cold-box binder, with the remainder using shell core and cold-set phenolic urethane binders. This foundry's casting weights ranged from 2 to 450 pounds.

The difference between response to Foundry F8 samples (see Figure 18) and the previous seven was that response to fresh waste sands was, on average, higher than that to system sand. This was especially noticeable for two of the fresh waste samples. It is possible that waste sand leachates contained some contamination stemming from core binders which was eliminated as part of the sand recycling processes (e.g., removed with the fines or core butts) and therefore not present in the system sands. Additional Microtox™ testing could be used to determine whether the two samples which caused relatively high inhibition of light production were typical of waste sand samples.

7.3.3.9 Foundry F9

Foundry F9 was a gray iron foundry. This facility's average daily metal casting level at 600 tons required 300 tons of new molding and core sand per day. A cold-box phenolic urethane resin was used for 95% of this plant's cores, with the remainder produced using a hot-box phenolic procedure. Casting sizes typically ranged between 80 and 550 pounds.

Most of the Foundry F9 system sand samples caused responses greater than the virgin sand average (see Figure 19). This response seemed to increase over the period of testing. As shown in Figure 20, fresh waste sand samples caused even higher responses than system sands, similar to the response to Foundry F8 leachates.

As the only visible difference between this foundry and the previous eight foundries was the use of hot-box binders for a fraction of their cores, it can be hypothesized that this was the cause of the increased inhibition levels.

7.3.3.10 Foundry F10

Foundry F10 was a relatively large gray iron foundry, casting ~230 tons of metal per day. Daily sand use at this facility averaged about 240 tons per day. Casting weights ranged from 100 to 2,500 pounds. Eighty percent of the binder chemicals used were phenolic urethane cold-box resins; the remainder were hot box resins.

Figure 21 displays system and fresh waste sand results for Foundry F10. Response to system sand was not significantly different from virgin sand average levels. Response to fresh waste sands varied greatly, even over a short period, but was very high for three of the four samples. The use of hot box

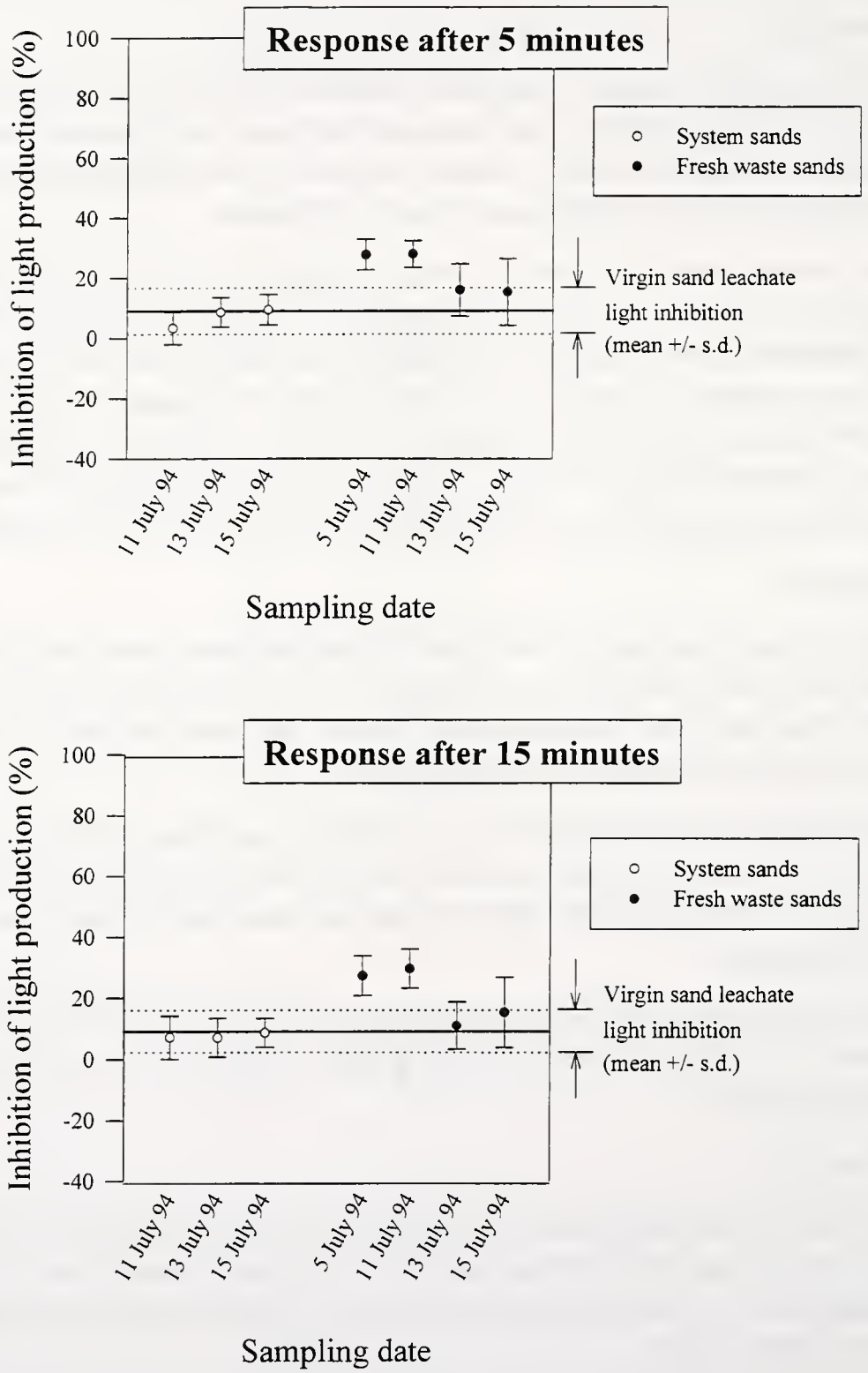
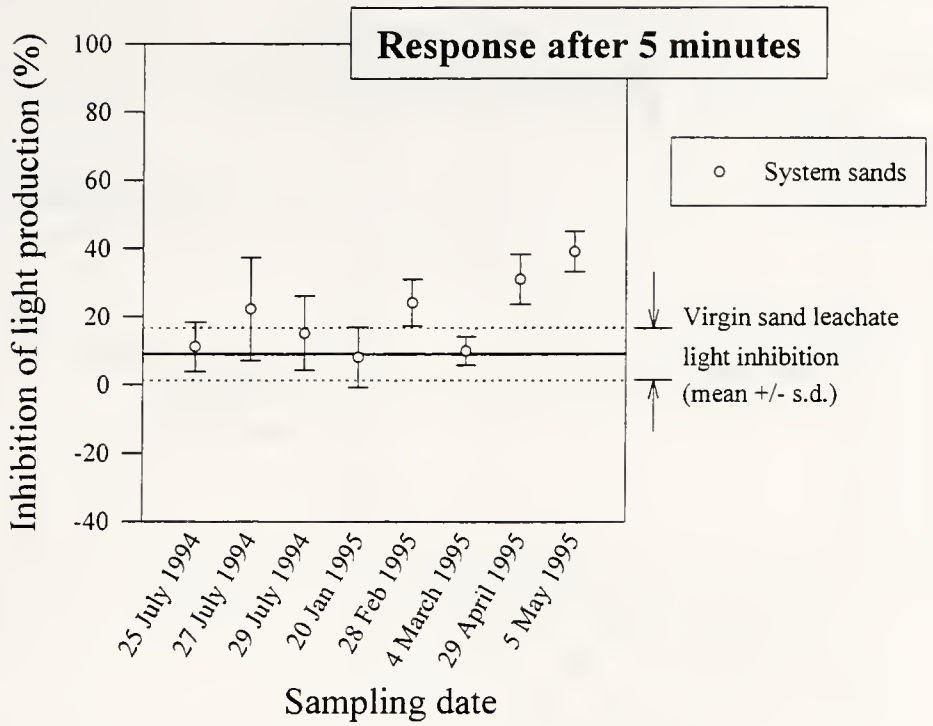


Figure 18: Microtox™ Response to Foundry F8 Sands



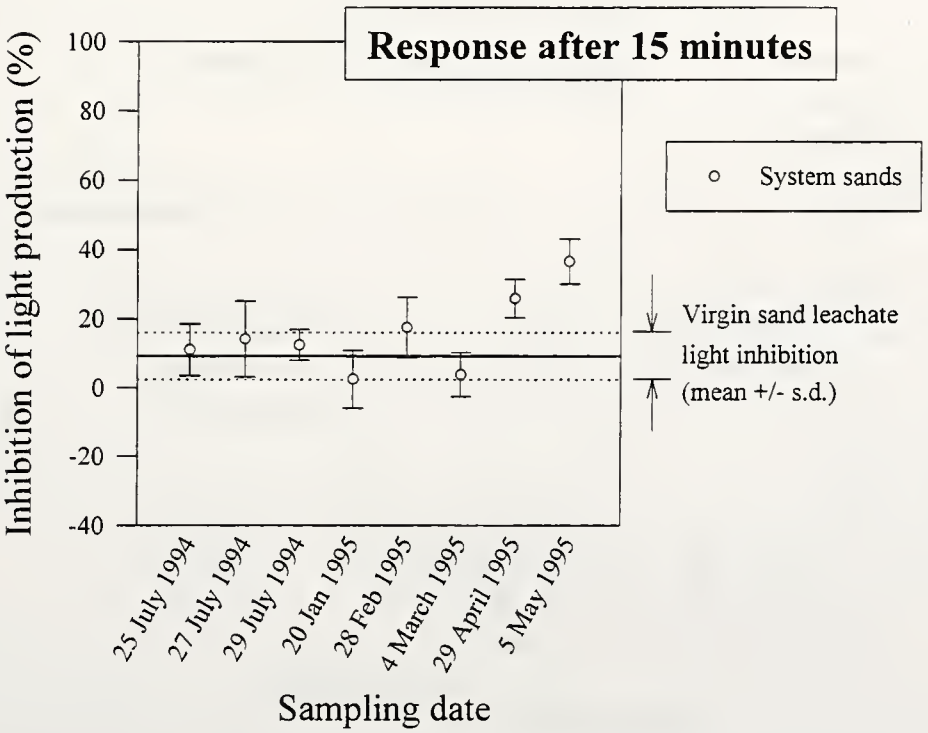


Figure 19: Microtox™ Response to Foundry F9 System Sands

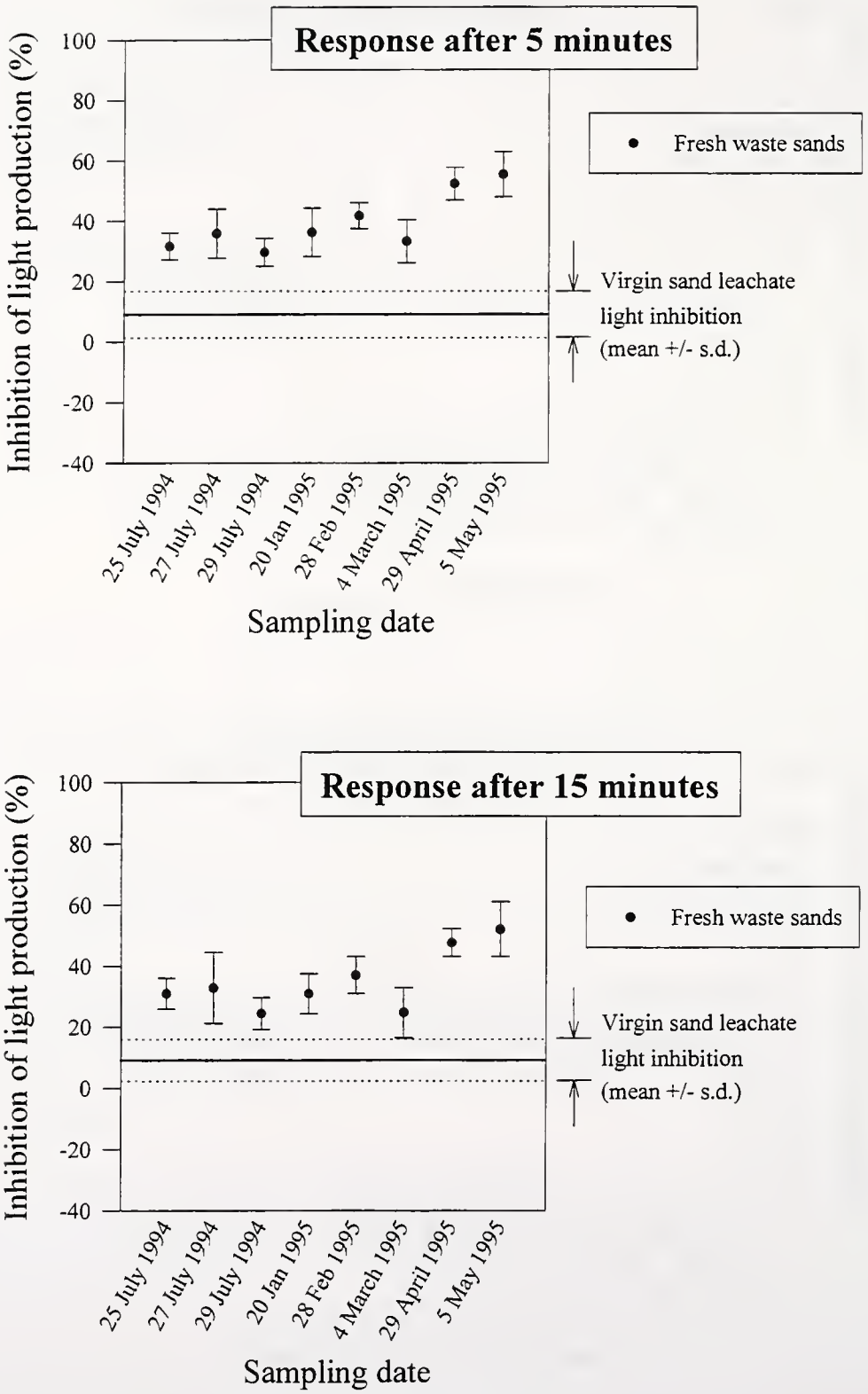
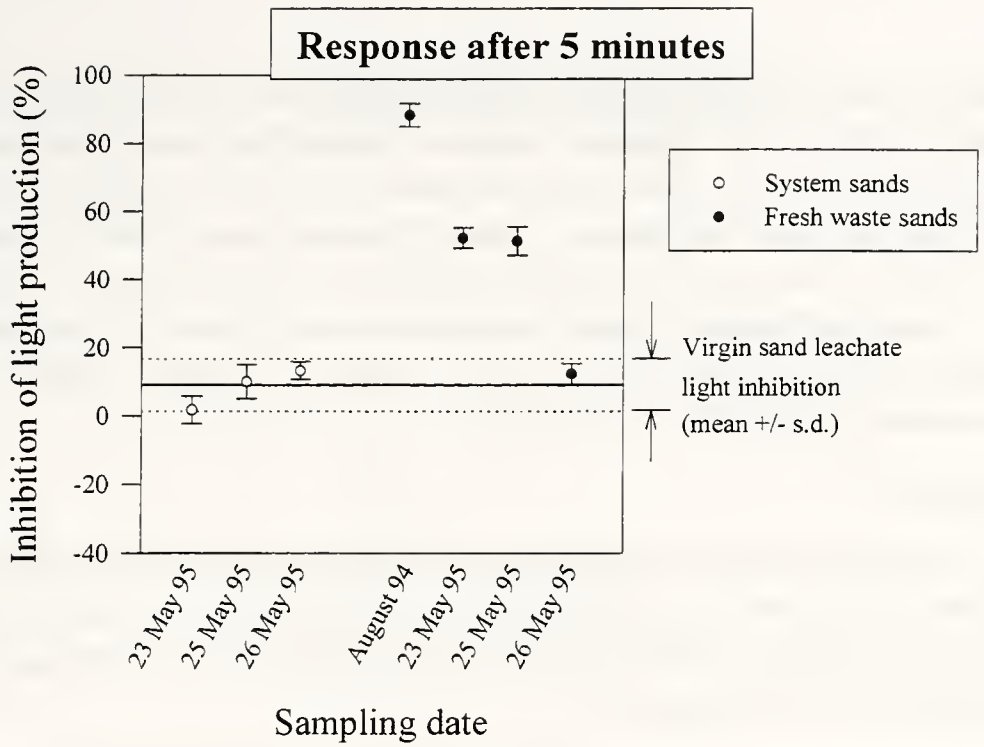


Figure 20: Microtox™ Response to Foundry F9 Fresh Waste Sands



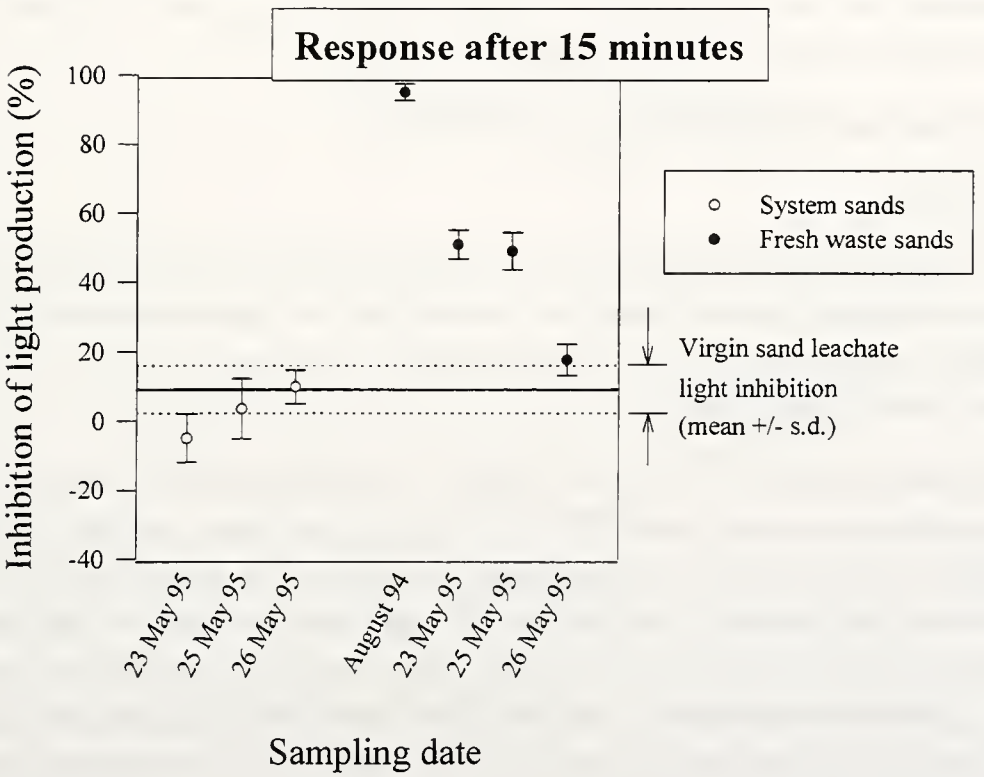


Figure 21: Microtox™ Response to Foundry F10 System and Fresh Waste Sands

binders, again followed by noticeable inhibition of light production, supports the hypothesis that this type of binder, or oxidation products thereof, remains on the sand long enough and at high enough concentrations to have a negative effect on the sand leachates. Aged waste sands were taken from waste piles which had been built up over a period of several months; Figure 22 shows that Microtox™ response varied greatly but that the average was less than response to virgin sand leachates; no correlation with sampling depth or sample age existed. If significant contamination was indeed typical in Foundry F10 waste sands, contaminants may have volatilized or leached from most of the areas sampled for testing.

7.3.3.11 Foundry F11

Foundry F11 was a gray and ductile iron foundry, casting approximately 90 tons of metal per day. A chemical binder system, phenolic urethane cold-set, was used for mold sands and the majority of core sand (approximately 99%). Daily sand use was ~500 tons. This plant had a wide range in casting sizes, extending from 1 to 2000 pounds.

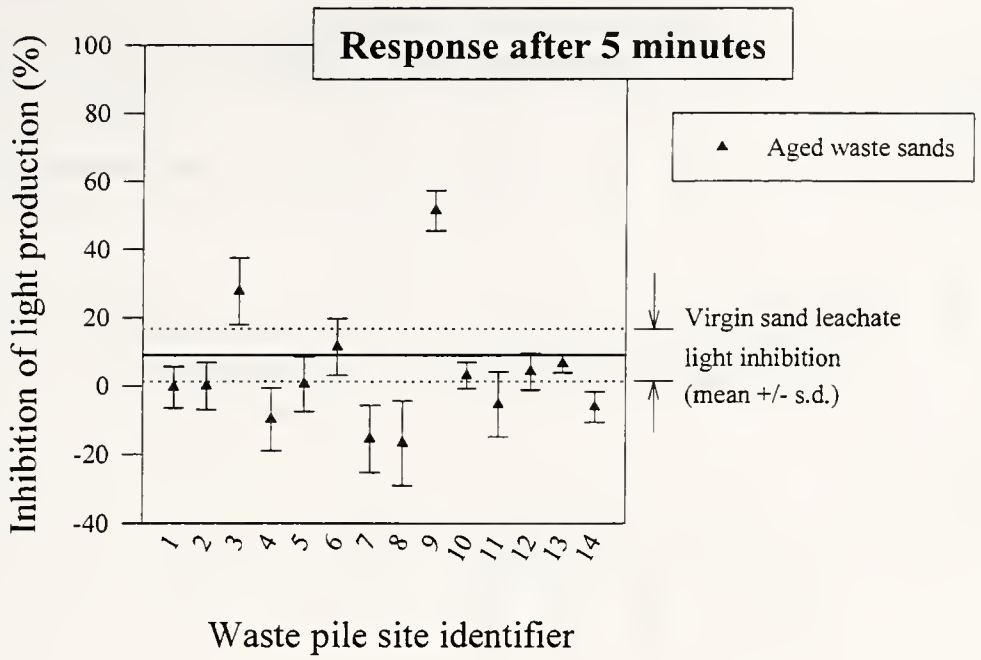
The only samples available were of waste sands. A distinct organic chemical smell was present in all samples; response was consistently high with respect to that to virgin sands, likely due to binder chemicals remaining on the sands after casting (see Figure 23).

7.3.4 Non-ferrous foundry operations

7.3.4.1 Foundry N1

Foundry N1 was a steel foundry which cast 130 tons of metal and used 950 tons of sand per day. As compared to the majority of gray and ductile iron foundries, this 'N1' operation produced fairly large castings, with an approximate range of 25 to 9000 pounds. The binders included cold-box phenolic urethane and sodium silicate systems.

A significant difference between iron and steel casting, aside from the different metals cast, was the temperature--steel is cast at approximately 2850 °F (1565 °C). One might guess that contamination due to organics would be decreased, due to the higher temperature. As seen in Figure 24, however, fresh waste sands from Foundry N1 all had relatively high levels of inhibition of light production. This behavior could stem from the use of sodium silicate binders or, more likely, from greater quantities of applied binder chemicals. It may also be that cores were so large that the temperature in the inner parts of the cores were not high enough to oxidize the binder chemicals. Due to the observation that the Microtox™ response did not increase with contact time, the inhibition of light production was likely due to organics rather than metals. This circumstance mirrors the results witnessed with the aforementioned iron foundries.



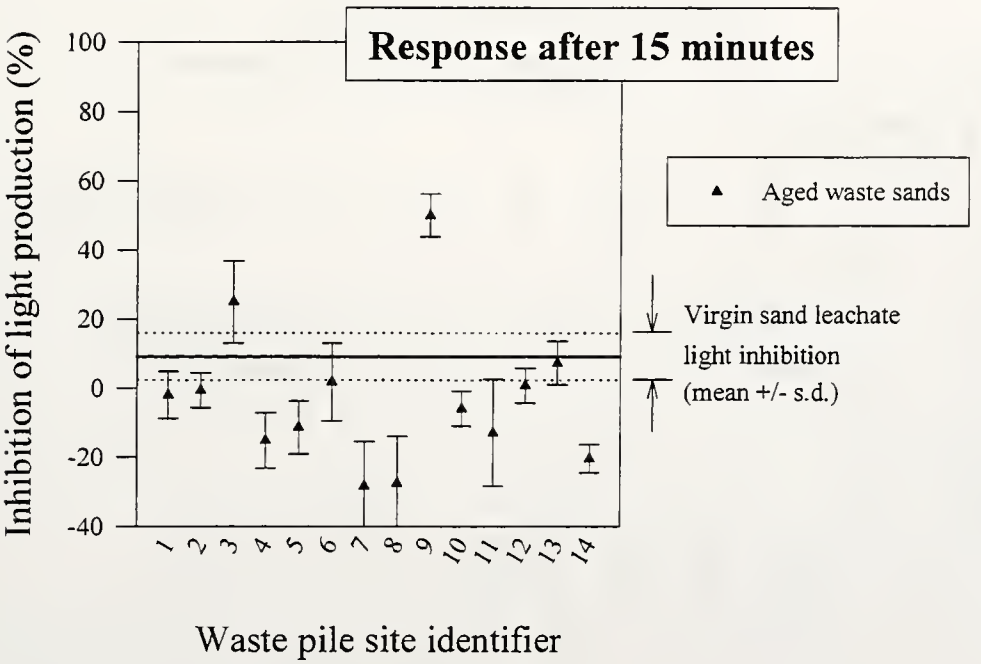
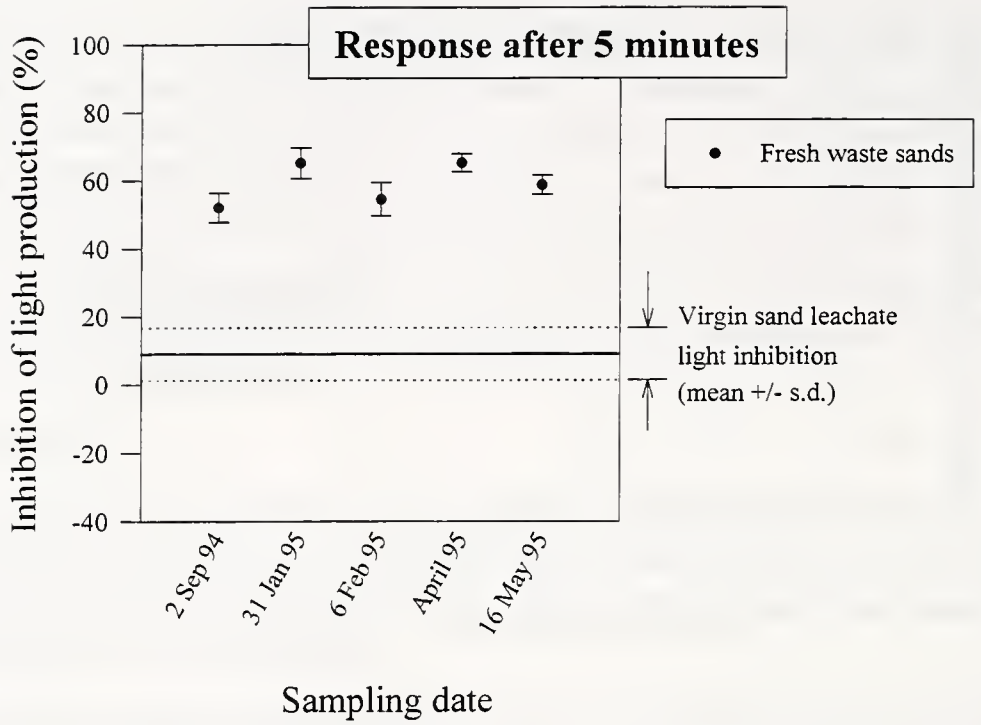


Figure 22: Microtox™ Response to Foundry F10 Aged Waste Sands



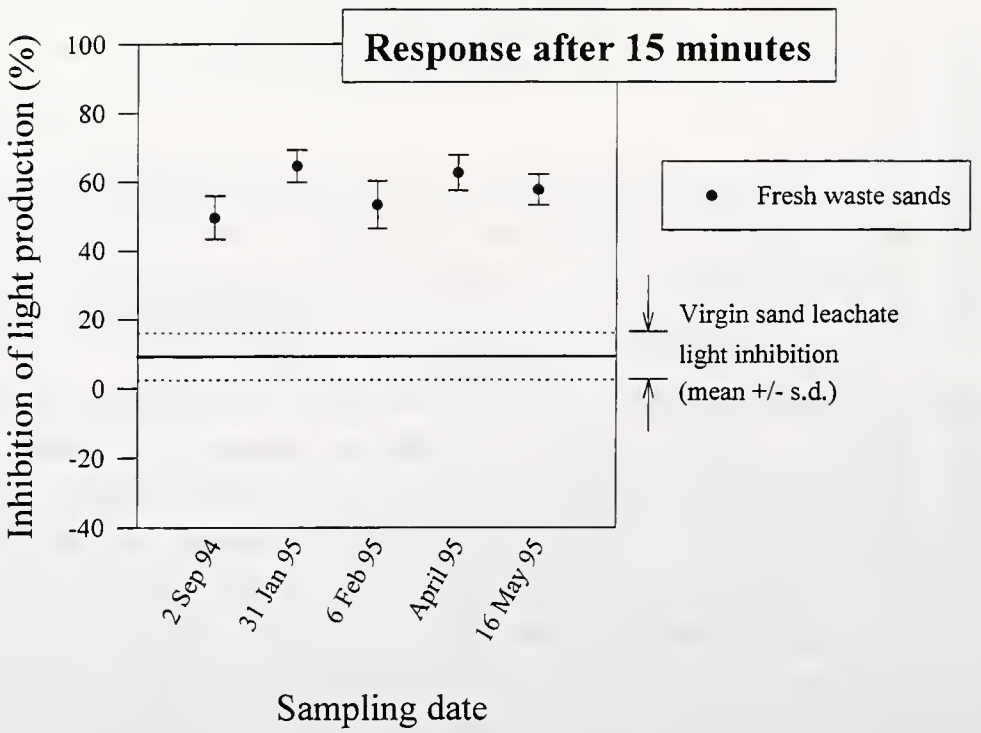


Figure 23: Microtox™ Response to Foundry F11 Sands

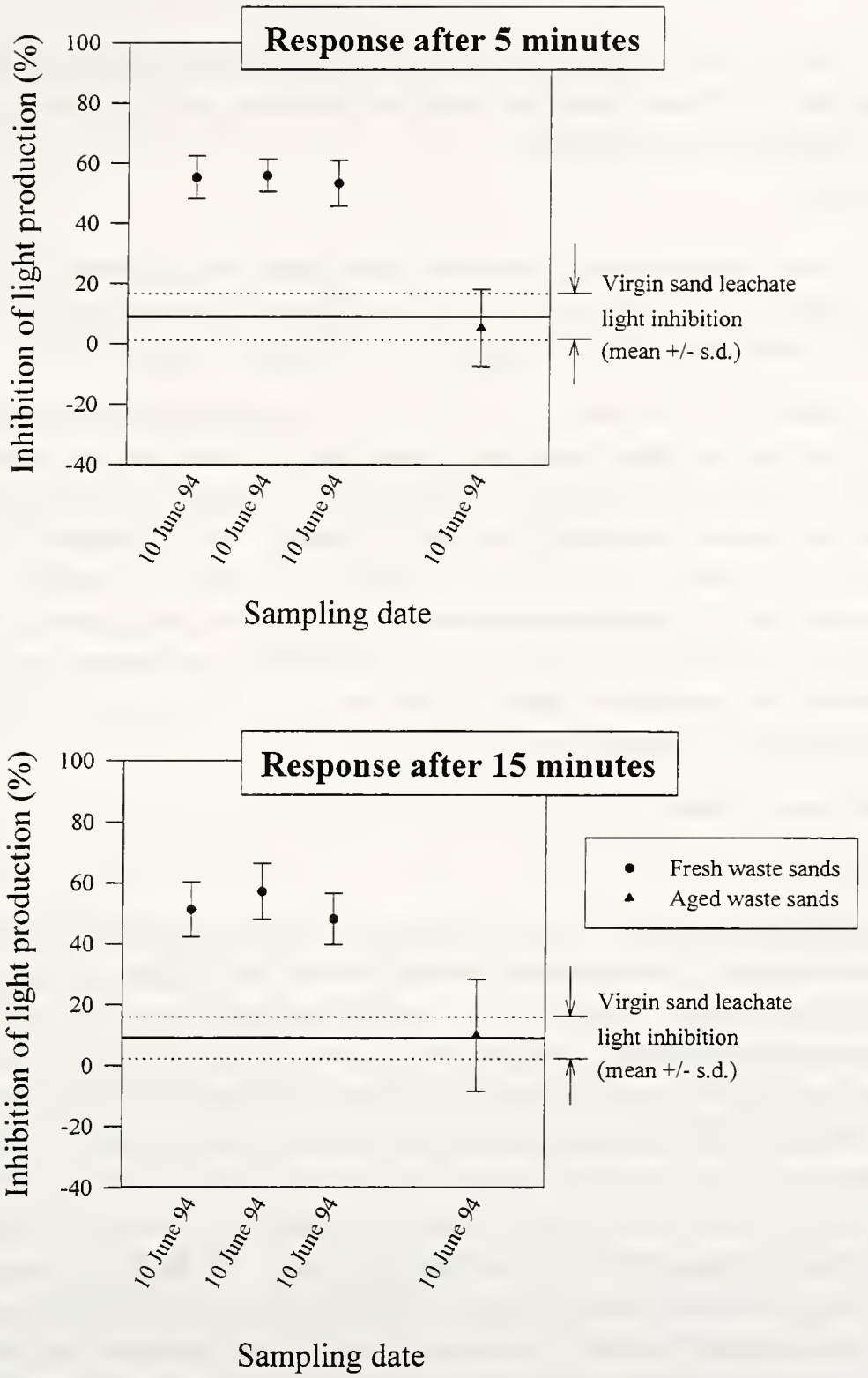


Figure 24: Microtox™ Response to Foundry N1 Sands

Foundry N1 disposes of its waste sands in a privately owned monofill. As response to aged waste sand leachates was very close to that of virgin sands, it is conceivable that the organic contaminants volatilized or leached out of the waste pile.

7.3.4.2 Foundry N2

Foundry N2 was an aluminum foundry, producing castings which range in weight from 16 to 35 pounds. The binder used at this facility (Acme-Borden '*Acme-Flow*') was based on a cold-box process. This foundry cast ~150 tons of metal each day, and used 125 tons of sand.

Aluminum is melted at a temperature of 1300 °F (700 °C). By comparison, this temperature is considerably lower than the melting point of iron. Consequently, the molds andcores break down to a much smaller extent during casting, necessitating the use of additional vibration or shaking to separate the sand from the castings after the metal has cooled. Much higher levels of organic contamination were expected, and the results of Microtox™ testing were consistent with such expectations (see Figure 25). Bacterial inhibition levels by system, fresh waste, and even aged waste sand leachates were consistently higher than had been seen in ferrous orsteel foundry sands. As with the iron foundries, this response was believed to have been due to metals, given the fact that there was no sizable increase in inhibition from 5 to 15 minutes.

7.3.5 Quality control results

7.3.5.1 Extraction controls

Microtox™ test results for extraction controls (NaCl solution without sand added) are presented in Figure 26. Mean Microtox™ responses were 5.5% and 6.5% for 5- and 15-minute tests, respectively. A surprisingly large variation in these values was observed (standard deviations 10.8% and 12.9%, respectively), especially for the last several tests; the reason for the variation, and for the relatively high response to some of the control samples, was unclear. This effect did not carry over to sand samples: no correlation between foundry sand response and control response existed. It was possible that the existence of a toxin in the NaCl solution was eliminated during the extraction procedure (adsorbed by the clays in the foundry sand, for example) or masked by the presence of salts of other constituents which were dissolved during the extraction procedure. This might also explain the low responses to many of the foundry sands compared to virgin sands samples, which would not contain the clays or ions potentially present in foundry sand samples. This hypothesis is as yet simply a possibility, but might be demonstrated through bioassay testing of non-inhibitory foundry sands to which toxins have been added (e.g., "spiked samples").

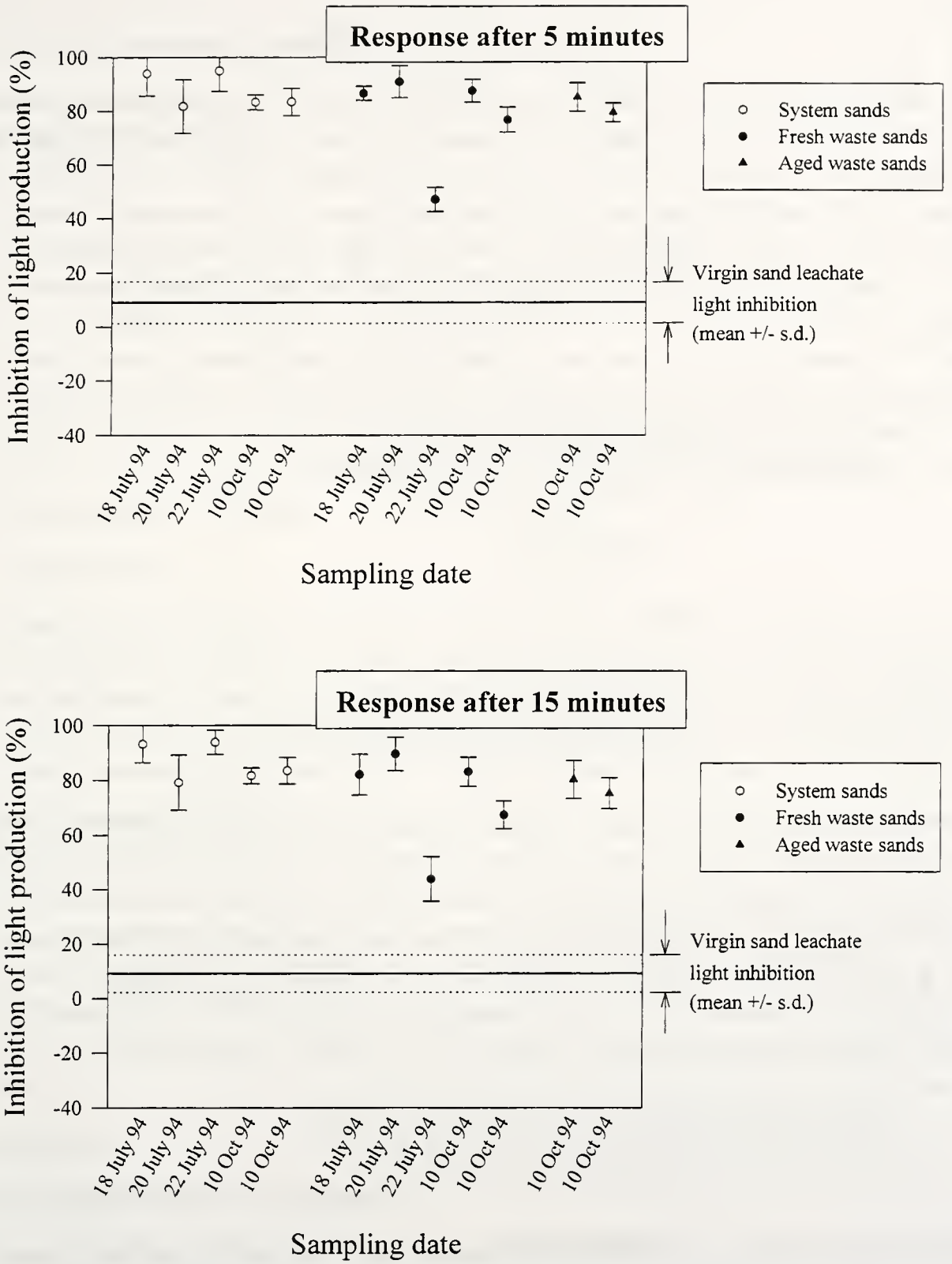


Figure 25: Microtox™ Response to Foundry N2 Sands

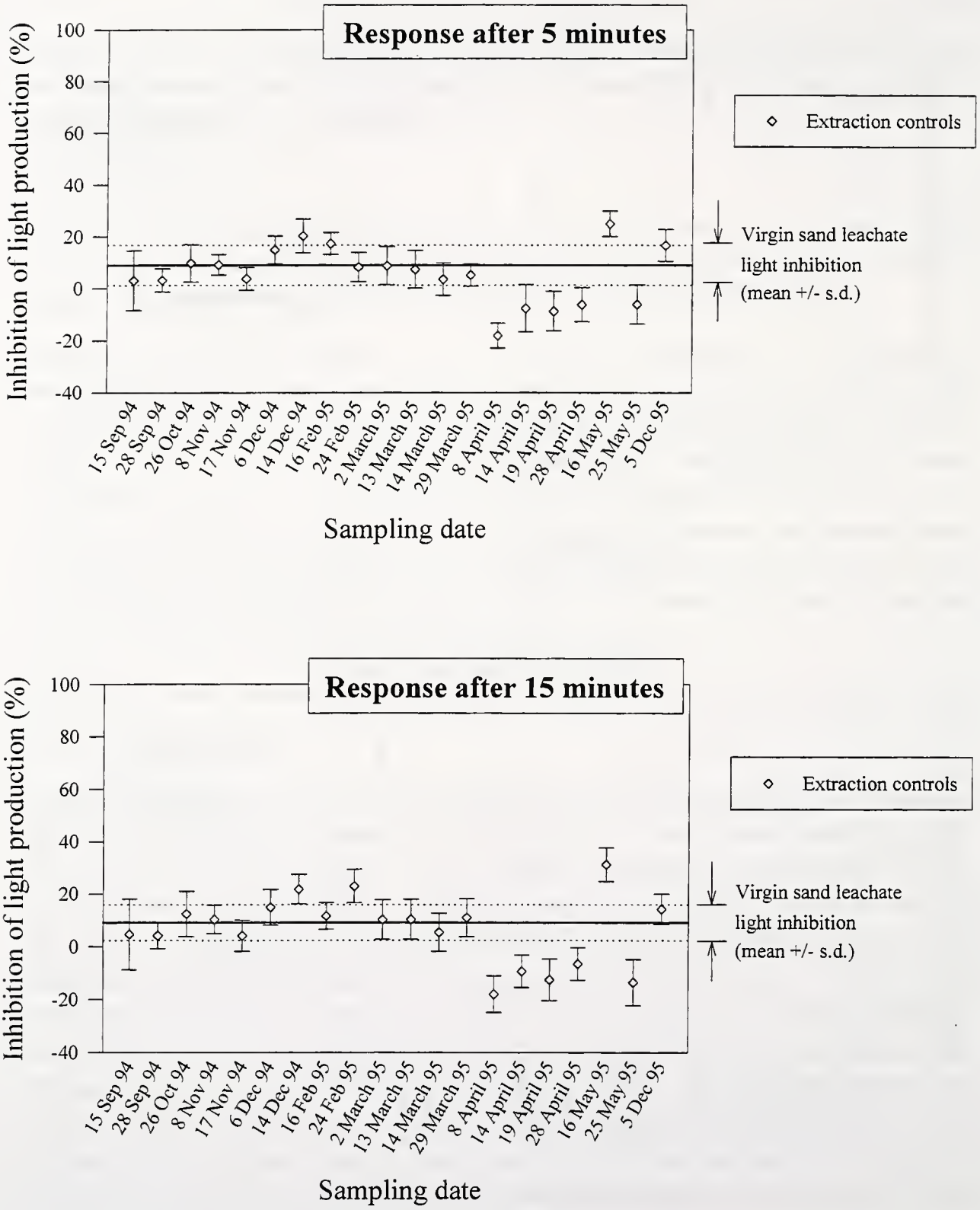


Figure 26: Microtox™ Response to Extraction Controls

7.3.5.2 Tests of organic standards

Figure 27 contains Microtox™ results for an organic standard (phenol, 10 mg/L) tested periodically during foundry sand testing. Testing is considered to be acceptably precise when a coefficient of variation (e.g., the standard of deviation of a group of tests, divided by the mean) of less than 20% is maintained (Microbics, 1992). As can be seen, the first data point, dated 7 October 1994, displayed a inhibition of light production almost twice that of the following five samples. The precision demonstrated by latter samples, however, suggests that the first value was due to an experimental error not repeated in later testing. Due to the fact that sand response did not display a similar variation, it is believed that the error can be attributed to an incorrect standard formulation rather than an error in the Microtox™ testing procedure. Ignoring the first measurement, the coefficient of variation was 6.7%, well within the criteria specified for acceptable precision. It should be noted that, in Figures 3 and 4, average and range of response shown were calculated using only the five data points considered to be accurate.

7.4 NITROTOX

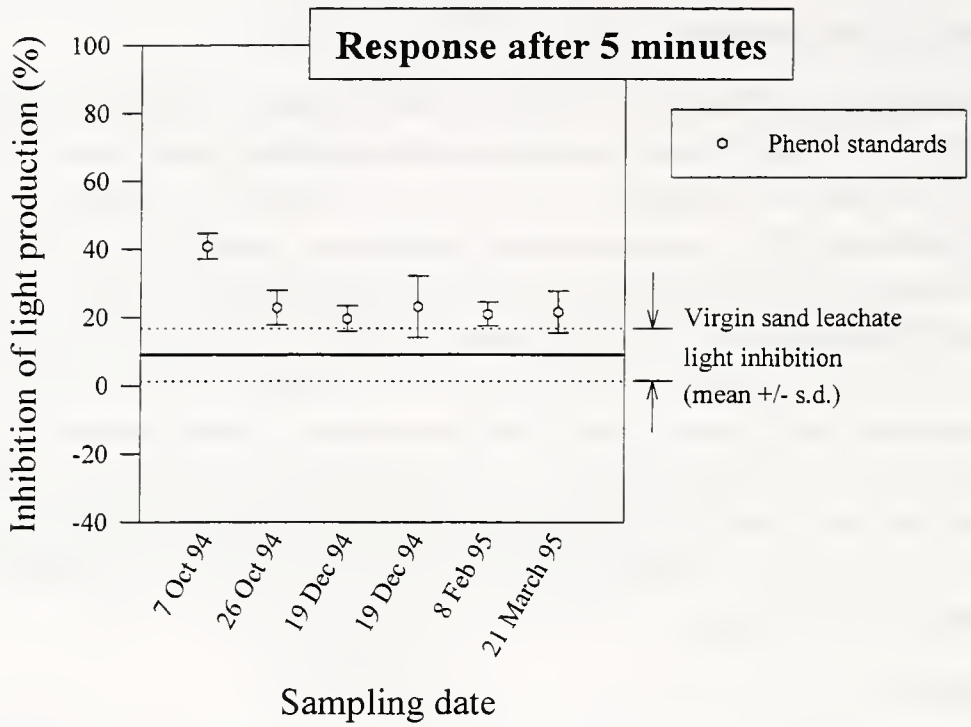
An exploratory series of experimental Nitrotox tests were also performed on a variety of virgin and ferrous foundry sand samples. In retrospect, these bioassay tests appeared to be relatively insensitive to any substances encountered in foundry sand leachates, as no response (e.g., decrease in production of MTT-formazan) was higher than approximately 20%. Furthermore, as seen in Figure 28, no correlation between Nitrotox and Microtox™ response values could be made.

Due to the marginal value of these preliminary results, a number of inherent problems with the original analytical protocol were belatedly recognized. In turn, substantial changes have been implemented with this Nitrotox procedure, leading to considerable improvements in this bioassay's response. At this point, therefore, the improved Nitrotox test has demonstrated a level of sensitivity at least comparable to, and perhaps even greater than, that of the Microtox™ assay. Since the nitrifying organisms used in the Nitrotox test are considered to be potentially even more sensitive than most other bacterial species, it is hoped that an optimized Nitrotox test will shortly provide useful data.

7.5 GC/MS

7.5.1 Leachate Sample Characteristics

Although inhibition of the Microtox™ organisms had been observed with two of the four tested sands (i.e., samples F9 and F11), the 'leachate' GC/MS results failed to identify measurable organics in any of these four samples. This circumstance can possibly be linked with either of two inherent analytical shortcomings. First, the levels of the leached organics may simply have been below the instrument's



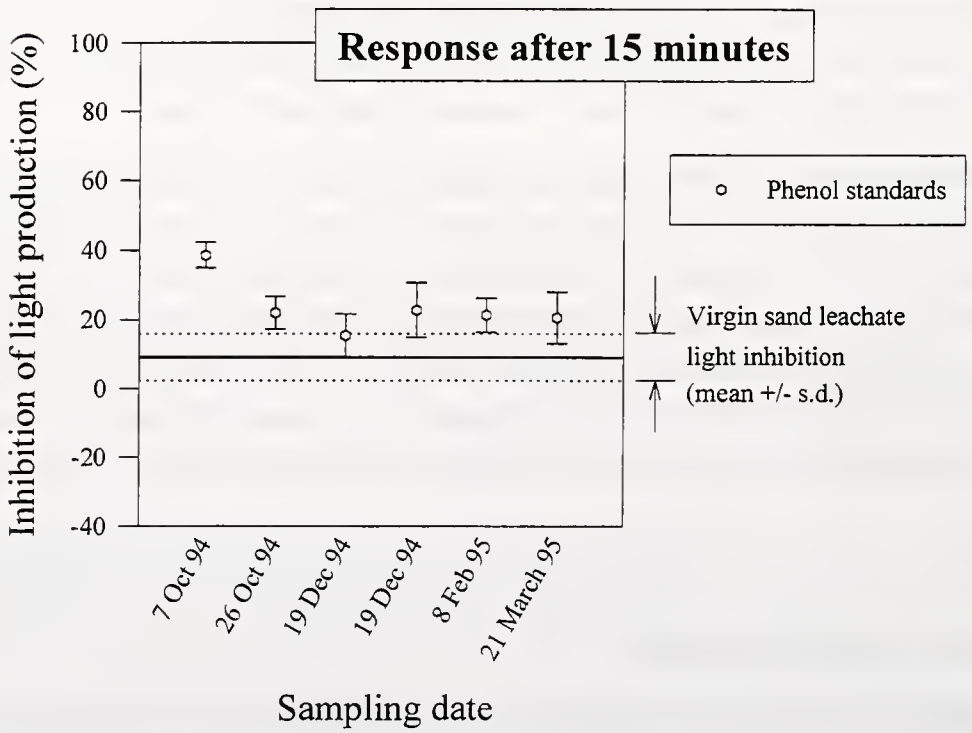


Figure 27: Microtox™ Response to Phenol Standards

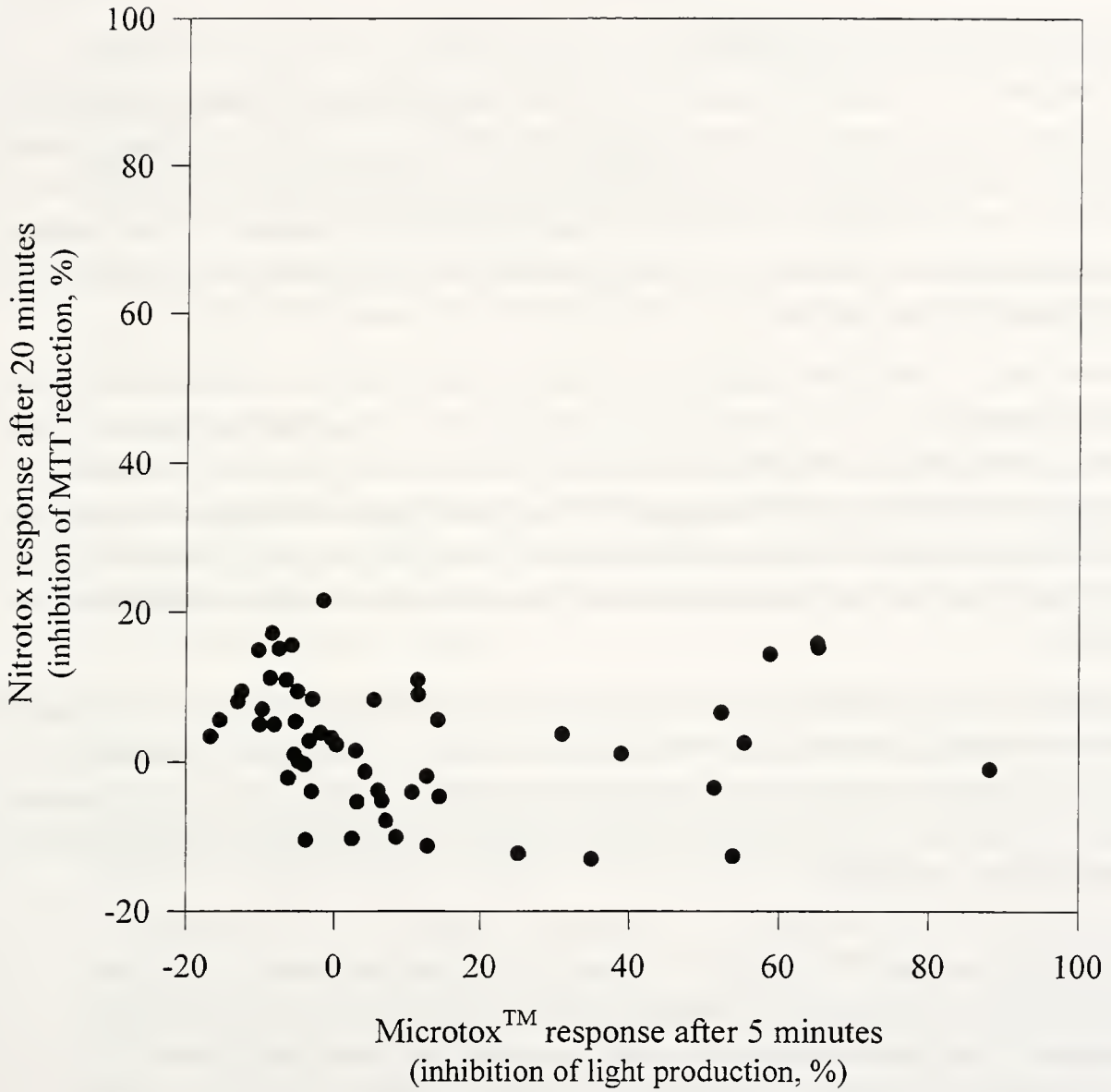


Figure 28: Toxicity Response Comparison: Nitrotox [20 min.] versus Microtox™ [5 min.]

limit of detection. Second, the released organics may have not been amenable to this analytical procedure...perhaps due to molecular size, configuration, etc. The latter rationale appears to be the more likely factor.

7.5.2 Off-Gas Sample Characteristics

As compared to the leachate measurements, off-gas testing of foundry sands generated distinct indications of the presence of released organics. For those sands in which the bioassay testing produced a 'clean' fingerprint (i.e., the virgin and F1 sands), there was only a nominal indication of an off-gas contaminant release. Both of these sands did exhibit the presence of a butoxyethanol compound. However, in retrospect, it was believed that this material represented an artifact of the sample preparation procedure.

The two sands for which bacterial inhibition had been previously observed, though, released off-gas organics whose form and concentration was distinctly different from the aforementioned 'clean' sands. Trimethylbenzene contaminants were found in each these off-gas streams. In addition, the F11 sample (which comparatively displayed the higher level of bioassay response) was also found to have released 2-ethoxyethyl acetate, as well as a number of additional organic contaminants bearing ring-related structures, including: naphthalene, methyl naphthalene, and methylbenzenes (both tetra- and penta-).

Admittedly, this information is semi-quantitative, but the overall impression is that of analytically reinforcing the ability of the bioassay test to identify suspect sands. At this point, there is simply not enough information available to specifically determine which, if any, of these off-gas contaminants might be responsible for the identified bioassay response. However, this correlation certainly warrants further consideration.

CHAPTER 8

CONCLUSIONS

1. The Microtox™ test can be effectively used to 'fingerprint' waste sands which might impose a negative environmental impact.

2. Microtox™ light inhibition by virgin sand leachates after 5 minutes averaged 9.0% (range -3.8% to 25.1%), and 9.15% (range -2.0% to 24.8%) after15 minutes.

3. Of the eleven (11) tested ferrous foundries, seven (7) showed little if any indication of a negative Microtox™ response, with no light inhibition significantly greater than that seen with virgin sands.

4. The leachates obtained from three (3) ferrous foundry operations exhibited average Microtox™ bioassay results for their fresh waste sands which were significantly above the response identified for virgin sand, thereby suggesting the possible presence of undesired contaminants. However, these results were erratic and had a level of variation between their high and low extremes which was noticeably more pronounced than had been the case with the aforementioned seven foundries.

5. One (1) ferrous foundry's leachates had a significant, and consistently negative, impact on Microtox™ bacterial light production as compared with virgin sand response.

6. Leachate from samples produced from the steel and aluminum foundries consistently caused inhibition of light production as compared with virgin sand response.

7. It appears that there is a correlation between the casting process options (e.g., chemicals used, size of casting, and casting temperature) and Microtox™ response. Specifically, leachates from sands wasted by foundries which utilized phenolic urethane cold-box and shell core binders did not usually cause inhibition of light production by the Microtox™ organisms relative to that of virgin sands. Leachates from sands with which hot-box core binders and from chemically bound mold sands, on the other hand, tended to inhibit light production by the Microtox™ bacteria.

8. The 'Nitrotox' nitrifier bioassay results did not correlate with Microtox™ response, and the new test did not appear to be sensitive to any contaminants present in foundry sand leachates. Although the Nitrotox and Microtox™ tests did not function similarly or complementarily in this study, results subsequently developed with an altered Nitrotox protocol indicate the

potential for greatly increased sensitivity to contaminants, including heavy metals.

9. Gas chromatography/mass spectrophotometry was used to preliminarily identify a number of volatile organic contaminants which might be encountered with these waste foundry sands. Although the extent of this testing effort was limited, these results provided a promising indication that additional GC/MS testing of WFS off-gases could be used to determine and quantify potentially troublesome organics (i.e., those contaminants able to cause negative bioassay responses).

10. In summary, Microtox™ testing was able to fingerprint sands with questionable environmental qualities, these same sands would likely pass TCLP and neutral leachate tests for Type III or Type IV classification. Microtox™ testing therefore provides an effective reassurance regarding the character of waste foundry sands and their potential for a negative effect on the environment (and the liability associated therewith).

11. Overall, this innovative bioassay test appears to offer an efficient and expedient approach to testing waste foundry sands regarding their potential suitability for constructive reuse applications.

CHAPTER 9

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APPENDIX

PERMANENT PATTERN/EXPENDABLE MOLD CASTING PROCESSES

Inorganic Binder Options (2 each)

Name: Greensand

Binder: Clays: Montmorillonites, western (Na^+) and southern (Ca^{++}). (5-7%).

Additives: Water (2.5-3.5%); starch (0.5%); and coal dust (≤3%) to improve surface finish

Mechanism: Surface interactions between clay-coated sand particles.

Name: Alumina phosphate

Binder: Acidic, water-soluble alumina phosphate liquid resin

Catalyst/Hardener: Acidic powdered metal oxide hardener such as magnesium oxide

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Cold Set/No-Bake (Organic) Binder Options (7 each)

Name: Furan binders

Binder: Liquid furfuryl alcohol resin (1%)

Additives: Urea, phenol, formaldehyde, others

Catalyst/Hardener: Phosphoric acid, aryl sulfonic acid such as benzene sulfonic acid (BSA) or toluene sulfonic acid (TSA), or sulfuric acid (15-45% of resin weight)

Name: Phenolic binders

Binder: Phenolic resole resins (1-2%)

Additives: Phenol, formaldehyde, others

Catalyst/Hardener: Sulfonic acid such as BSA or TSA (20-45% of resin)

Name: Ester cured phenolic

Binder: Phenolic resole resin & liquid ester co-reactants

Possible Trade Name: Borden Alphaset

Name:	Alkyd (oil) Urethane
Binder:	A: Alkyd oil resin (1-2% of sand weight)
	C: Polymeric isocyanate (18-20% of A)
Catalyst/Hardener:	B: Liquid amine/ metallic catalyst (2-10% of A)
Mechanism:	(1) Part C reacts with part A at a rate controlled by B
	(2) Oxidation polymerization of alkyd resin by atmospheric O_2,accelerated by metals in part B

Name:	Phenolic urethane
Binder:	I. Phenol formaldehyde resin (0.7 to 2.0% of sand weight)
	II. Polymeric isocyanate (0.7 to 2.0% of sand weight)
Catalyst/Hardener:	Liquid amine catalyst (0.4 to 0.8% of Part I)
Possible Trade Name:	Pepset
Mechanism:	Phenol formaldehyde hydroxyl groups react with isocyanate to form urethane bonds

Name:	Polyol urethane
Binder:	I. Polyol
	II. Polymeric isocyanate
Possible Trade Name:	Novathane

Name:	Sodium silicate-Ester cured
Binder:	Liquid sodium silicate
Catalyst/Hardener:	Liquid organic ester such as glycerol diacetate or triacetate (10-15% of silicate by weight)
Mechanism:	Organic esters hydrolyze to react with sodium silicate to make silica gel.

Cold Box (Organic) Binder Options (9 each)

Name: Phenolic urethane

Binder: I. Phenol formaldehyde resin

II. Polymeric isocyanate

Catalyst/Hardener: Gaseous TEA (triethylamine) or DMEA (dimethyl-ethylamine)

Possible Trade Name: Ashland Isocure

Name: Furan-SO_2

Binder: I. Furan resin (e.g., furfuryl alcohol/ formaldehyde)

II. Peroxide [e.g., methyl ethyl ketone peroxide, MEKP] (20-50% of resin weight)

III. Silane

Catalyst/Hardener: SO_2 gas

Possible Trade Name: So-Fast, Hardox, or InstaDraw

Mechanism: The SO_2 gas is oxidized by the peroxide to sulfur trioxide, which dissolves in the water associatedwith the resin to form sulfuric acid which polymerizes the resin.

Name: Epoxy-SO_2

Binder: A. Modified epoxy resin with an aromatic peroxide

B. Epoxy resin with acrylic modifiers

Additives: Phenol formaldehyde

Catalyst/Hardener: SO_2 gas

Possible Trade Name: Rutapox

Name: Free-radical cure

Binder: I. Vinyl unsaturated urethane oligomer

II. Organic peroxide

III. Vinyl silane adhesion promoter

Catalyst/Hardener: SO_2 gas

Possible Trade Name: FRC

Mechanism: The SO_2 gas breaks down peroxide to produce free radicals, causing polymerization.

Name: Ester cured phenolic

Binder: Water-soluble alkaline phenolic resole (1.5% of sand weight)

Catalyst/Hardener: Methyl formate vapor

Possible Trade Name: Borden Betaset

Name: Ecolotec

Binder: Phenolic resole complexed with an oxyanion such as borate

Catalyst/Hardener: CO_2 gas

Possible Trade Name: Ecolotec

Mechanism: The CO_2 gas dissolves to produce carbonic acid, neutralizing the alkali in the system producing a complex of the resole and the borax

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Name: Polyacrylic-CO_2

Binder: I. Sodium polyacrylate (3-3.5%)

II. Calcium hydroxide (1-1.5%)

Catalyst/Hardener: CO_2 gas

Possible Trade Name: Polidox

Mechanism: The CO_2 gas causes a reaction between the CaOH and the polyacrylate.

Name: Redset

Binder: A. A liquid resorcinol formaldehyde polymer

B. Gaseous methylal

Catalyst/Hardener: Acid catalyst

Possible Trade Name: Redset

Mechanism: The acid and polymer are mixed with the sand; the gas is blown in with the sand at 40 °C

Name: Silicate-CO_2

Binder: Liquid sodium silicate (3-6%)

Additives: Coal dust or refractory wash to improve surface finish; clays or organics such as sugars to improve sand breakdown

Catalyst/Hardener: CO_2 gas (1-2 lb. gas per 100 lb. sand)

Mechanism: (1) Dehydration increases binder viscosity

(2) $Na_2SiO_3 + 2H_2O + CO_2 \rightarrow Si(OH)_4 + Na_2CO_3$; monosilicic acid monomer polymerizes to gel-like material

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Heat Activated (Organic) Options (3 each)

Name: Hot Box

Binder: Furfuryl alcohol and/or phenol based; contain urea and formaldehyde

Catalyst/Hardener: Acid catalyst

Mechanism: Wet mixture is blown into a heated core box (220 to 245°C; 425 to 475°F), enabling rapid cure within 10 to 30 seconds

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Name: Warm Box

Binder: Cold blended furfuryl alcohol monomers

Catalyst/Hardener: Copper salts, based on aromatic sulfonic acids (20-35% of binder weight)

Mechanism: Cured at 150 to 220 °C (300 to 430 °F)

Name: Shell Molding

Binder: "Novolak" phenol formaldehyde resins (2-5% of sand weight)

Additives: Calcium stearate (lubricant) (2-5% of resin weight);Vinsol (plasticizer) (10% of resin weight); iron oxide

Catalyst/Hardener:	Hexamethylene tetra-amine ("hexamine" or "hexa") curing agent(15% of resin weight)
Mechanism:	Hexamethylene breaks down to release formaldehyde, which links the Novolak chains together at temperatures of 260 to 300 °C(500 to 570°F)

Name:	Core Oil
Binder:	Saturated fat oils
Additives:	Oxygen sources (perborates, percarbonates, permanganates, or peroxides), and solvents (turpentine, kerosene, mineral spirits)

Name:	Air Set
Binder:	Various oil resins

Sources: Clegg (1991) and FM&T (1993).

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